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# Small-angle scattering of dense, polydisperse granular porous media: computation free of size effects

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Small-angle X-ray and neutrons scattering is a widespread experimental tool for the investigation of the microstructure of random heterogeneous materials. Validation of (computer-generated) model microstructures often requires the numerical computation of the scattering intensity, which must be carried out with great care due to finite size effects. In this paper, a new method for this computation is presented. It is superior to previously existing methods for three reasons. First, it applies to any type of microstructures (not necessarily granular). Second, closed-form expressions of the size effects inherent to the proposed method can be rigorously derived and removed (in this sense, our method is free of size effects). Third, the complexity of the new algorithm is linear and the computation can easily be updated to account for local changes of the microstructure, while most existing algorithms are quadratic and any change of the microstructure requires a full recomputation.

The present paper provides full derivation and validation of this method. Application to the computation of the scattering intensity of dense, polydisperse assemblies of spheres is then presented. A new, simple algorithm for the generation of these dense configurations is introduced. Finally, the results are critically reviewed in the perspective of hardened cement pastes.

## I. INTRODUCTION

In materials science, numerical simulation of physical or mechanical phenomena in confined spaces (such as diffusive transport, convective transport or macroscopic deformation under applied macroscopic stress) often requires a full three-dimensional geometrical model of the heterogeneous material under consideration.

Since few experimental techniques provide direct access to the microstructure, one is often reduced to generating a synthetic, “realistic” microstructure, based on some knowledge of the material. Two approaches can be adopted to carry out this generation.

In mimetic simulations, an attempt is made at reproducing the physical and/or chemical phenomena involved in the elaboration of the real material. Early examples of such approaches are the generation of model silica aerogels by diffusion-limited cluster-cluster aggregation [1], and model porous glasses by molecular dynamics simulations [2, 3].

An alternative approach is the reconstruction of 3D models from limited microstructural information. In this approach, available experimental characterizations such as two-point correlation functions are used as constraints for the numerical model to be generated, the resulting cost-function being minimized by e.g. simulated annealing [4–6], maximization of the entropy [7] or genetic algorithms [8]. Reverse [9] and hybrid reverse [10] Monte-Carlo techniques can also be considered as constrained reconstructions.

Regardless of the actual approach used to create the model, consistency with all available experimental characterizations of the real material must subsequently be verified in order to assess the reliability of the model.

Small-angle X-ray and neutron scattering experiments are attractive tools for the investigation of the microstructure of disordered media. Indeed, they operate on macroscopic samples and provide quantitative 3D information at length-scales between 1 and 100 nm, while keeping sample preparation to a minimum. These experiments are therefore often used to carry out the validation of generated model geometries. For example, the structure factor (which is closely related to the scattering intensity) of silica aerogels is computed a posteriori in [1]. In [10], the reconstruction of porous carbons results from the minimization of a hybrid energy, made of the true energy of the system and the discrepancy between the actual and expected structure factors. In [11], reconstruction of amorphous material models is constrained by the experimental structure factor and gas adsorption data. In the last two examples, the structure factor constrains the reconstruction; it must therefore be computed at each step of the optimization algorithm.

Obviously, checking the computational model against experimental scattering intensity data requires that the small-angle scattering spectrum of this model be computed. Such a computation is generally difficult, since the practical size of model microstructures is rather small, compared to real samples. This limitation induces cut-off effects in real space, which in turn result in many artifacts in Fourier space (where the small-angle scattering experiment actually takes place).

In order to control these artifacts, non-trivial techniques must be invoked to carry out the computation (see the

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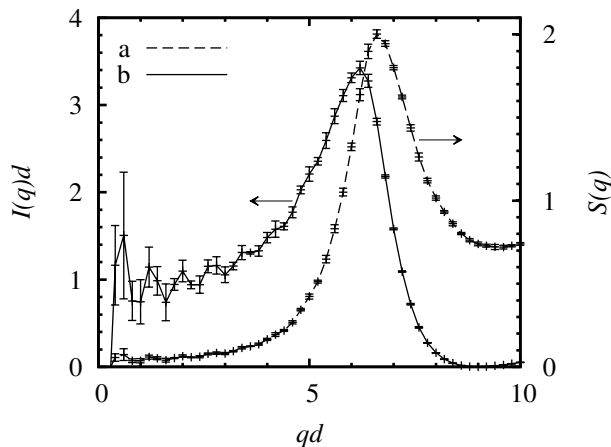


FIG. 1. Even for loose packings of equilibrium monodisperse hard spheres, state-of-the-art calculations of the scattering intensity can lead to spurious oscillations at low- $q$ . In the present example, four configurations of 4000 hard spheres, with density  $f = 0.4$  (volume fraction of solid) are considered. The average structure factor  $S(q)$  (a) is computed with the method of Salacuse *et al.* [12]. The result is very satisfactory, even at low- $q$ . This is not true of the scattering intensity  $I(q)$  (b); indeed, multiplication by the modulus-squared of the form factor amplifies the low- $q$  oscillations. Both  $q$  and  $I(q)$  have been made dimensionless through multiplication by the diameter  $d$  of the particles; furthermore,  $\Delta\rho = 100d^{-2}$ .

review in section II of this paper). However, figure 1 shows that some artifacts remain, even with existing state-of-the-art techniques. For dense, polydisperse configurations, which are addressed in this paper, these artifacts are even more pronounced.

This led us to derive a new technique for the computation of the small-angle scattering spectrum of a model microstructure. This method is presented in section III. The resulting spectrum is not free of artifacts; however, these artifacts are controlled, since they result in the true scattering intensity being convolved with a known kernel. Besides, a rigorous method is proposed for their removal. The new method is general, in the sense that it applies to any type of geometry. In the present paper, it is specialized to granular media, and validated against reference data computed on very large systems.

In section IV, the scattering intensity of dense polydisperse (log-normally distributed) granular media is then computed with this new, validated method. A simple but robust method is first proposed for the generation of the configurations (see section IV A). It is shown that even for relatively wide particle-size distributions, the resulting spectra exhibit a marked correlation peak. To the best of our knowledge, this result –though expected– has never been demonstrated before by means of computer simulations.

Section V closes this paper with a discussion on the scattering intensity of cementitious materials. The microstructure of calcium-silicate hydrates C-S-H, one of

the main hydration products of cement pastes, is still a matter of debate (in the remainder of this paper, standard notation from the cement industry will be adopted: C-S-H is a shorthand for calcium-silicate hydrate, with  $C \equiv \text{CaO}$ ,  $S \equiv \text{SiO}_2$ ,  $H \equiv \text{H}_2\text{O}$ ). Among the numerous models which can be found in the literature, the so-called globular model is probably the most popular. Based on small-angle scattering experiments by neutrons [13, 14], this model describes the C-S-H phase as an assembly of near-spherical particles, about 5 nm in diameter. Over the years, it has become overwhelmingly popular, and gave rise to a colloidal model of C-S-H [15–17]. The interest for this model has recently been renewed, since other experimental results, such as nano-indentation [18–20], or molecular simulations [21], can be interpreted in the light of the colloidal model of C-S-H. Our analysis suggests that only a very wide globule size distribution can account for the typical small-angle scattering spectrum of cement pastes (see figure 16). This raises the question of the origin of such a wide size distribution.

## II. COMPUTATION OF THE SCATTERING INTENSITY: STATE OF THE ART

Even with efficient procedures (see e.g. IV A), computer generated numerical samples are necessarily of very limited extent. In the present work, the typical size of the simulation box is about twenty times the average size of the particles. This is much smaller than the macroscopic samples usually considered in real small-angle scattering experiments, and pronounced boundary effects are therefore to be expected.

Several methods have been proposed in the past to reliably compute the scattering intensity of a numerical sample. These methods are reviewed in section II B, where it is shown that they do not fulfill the requirements of the present work.

First, in section II A, the general equations governing small-angle scattering of X-rays and neutrons by heterogeneous media are recalled. We do not intend to provide a full account of the small-angle scattering theory; only the essential equations to be used in the remainder of this paper are gathered here (the reader is referred to standard text-books for a more thorough review [e.g. 22, 23]).

### A. General equations

In a small-angle scattering experiment, the amplitude  $A$  of the scattered wave is proportional to the Fourier transform of the local scattering-length density  $\rho$

$$A(\mathbf{q}) = \int_{\mathbf{x} \in \Omega} \rho(\mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{x}) d^3\mathbf{x}, \quad (1)$$

where  $\mathbf{q}$  is the scattering-vector, and  $\Omega \subset \mathbb{R}^3$  is the domain occupied by the sample; all prefactors have been omitted,

as they are irrelevant to the present work. The absolute scattered intensity  $I(\mathbf{q})$  is then proportional to the square of the modulus of the amplitude

$$I(\mathbf{q}) = \lim_{V \rightarrow +\infty} \frac{1}{V} A(\mathbf{q}) A^*(\mathbf{q}), \quad (2)$$

where  $V = |\Omega|$  is the volume of the sample, and the above limit corresponds to the thermodynamic limit.

Following Debye *et al.* [24], it is convenient to introduce the fluctuations  $\eta(\mathbf{x}) = \rho(\mathbf{x}) - \langle \rho \rangle$  of the scattering-length density, where angle brackets denote ensemble averages. Then (1) reads

$$A(\mathbf{q}) = \int_{\mathbf{x} \in \Omega} \eta(\mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{x}) d^3\mathbf{x} + \langle \rho \rangle \int_{\mathbf{x} \in \Omega} \exp(-i\mathbf{q} \cdot \mathbf{x}) d^3\mathbf{x}.$$

We note that in the above equation, the last term depends only on the shape of the sample  $\Omega$ . It is usually omitted [25], since for samples large enough, it is negligible except for very small values of  $\mathbf{q}$  (it effectively reduces to a Dirac generalized function for infinitely large samples), which cannot be reached experimentally. It is therefore customary to write

$$A(\mathbf{q}) = \int_{\mathbf{x} \in \Omega} \eta(\mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{x}) d^3\mathbf{x}. \quad (3)$$

In “numerical experiments”, the size of the sample  $\Omega$  can no longer be considered as infinitely larger than the characteristic length-scale of the heterogeneities. Equations (1) and (3) are therefore not equivalent; this point will be addressed in section III B.

Gathering (2) and (3), and using the Wiener-Kintchine theorem, it is finally found that

$$I(\mathbf{q}) = \langle \eta^2 \rangle \int_{\mathbf{r} \in \mathbb{R}^3} \gamma(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3\mathbf{r}, \quad (4)$$

where  $\gamma(\mathbf{r})$ , first introduced by Debye *et al.* [24], is the normalized autocorrelation function of the fluctuations  $\eta(\mathbf{x})$

$$\begin{aligned} \gamma(\mathbf{r}) &= \frac{1}{\langle \eta^2 \rangle} \langle \eta(\mathbf{x}) \eta(\mathbf{x} + \mathbf{r}) \rangle \\ &= \frac{1}{\langle \eta^2 \rangle} \lim_{V \rightarrow +\infty} \frac{1}{V} \int_{\mathbf{x} \in \Omega} \eta(\mathbf{x}) \eta(\mathbf{x} + \mathbf{r}) d^3\mathbf{x}. \end{aligned} \quad (5)$$

In absolute scale, the scattering intensity appears as the Fourier transform of the autocorrelation of the scattering-length density fluctuations. In numerical experiments, because of the limited size of the sample,  $\gamma(\mathbf{r})$  cannot be computed for large values of the separation  $r = |\mathbf{r}|$  (typically, for  $r > L/2$ , where  $L$  is the size of the simulation box). It is therefore not possible to compute reliably its Fourier transform  $\hat{\gamma}(\mathbf{q}) = I(\mathbf{q})/\langle \eta^2 \rangle$  for small values of  $q = |\mathbf{q}|$  (typically  $q \leq s\pi/L$ , where  $s$  is of the order of the unity).

## B. Review of existing methods

In the present section, we review existing methods for the computation of the scattering intensity of granular media. For this type of microstructures, the following expression of the scattering amplitude  $A(\mathbf{q})$  is generally preferred over (3)

$$A(\mathbf{q}) = \sum_{\beta} \Delta\rho_{\beta} v_{\beta} F_{\beta}(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{x}_{\beta}), \quad (6)$$

where the sum is extended to all particles in the sample  $\Omega$ ,  $v_{\beta}$  is the volume of particle  $\beta$  centered at  $\mathbf{x}_{\beta}$ ,  $\Delta\rho_{\beta} = \rho_{\beta} - \rho_{\text{fluid}}$  its scattering length density contrast ( $\rho_{\beta}$ : scattering-length density of particle  $\beta$ ,  $\rho_{\text{fluid}}$ : scattering-length density of the saturating fluid), and  $F_{\beta}(\mathbf{q})$  its form factor [25]. For spherical particles

$$F_{\beta}(\mathbf{q}) = 3 \frac{j_1(qa_{\beta})}{qa_{\beta}}, \quad j_1(x) = \frac{\sin x - x \cos x}{x^2}, \quad (7)$$

where  $q = |\mathbf{q}|$ ,  $a_{\beta}$  is the radius of particle  $\beta$  and  $j_1$  denotes the spherical Bessel function of the first order and first kind.

Direct implementation of equation (6) (where the sum is now extended to all particles in the much smaller simulation box  $\mathcal{U}$ ), followed by the application of (2), (where no limit is taken) defines what will be called below the basic method. For isotropic, monodisperse configurations, the relevant formulae read

$$I(q) = \Delta\rho^2 f v F(q)^2 S(q), \quad (8a)$$

$$S(q) = \frac{1}{N} \sum_{\beta, \gamma=1}^N H(r_c - r_{\beta\gamma}) \text{sinc}(qr_{\beta\gamma}), \quad (8b)$$

where  $N$  is the total number of particles in  $\mathcal{U}$ ,  $f$  is their volume fraction,  $r_{\beta\gamma}$  is the center-to-center distance of particles  $\beta$  and  $\gamma$ ,  $r_c = L/2$  is the cut-off distance (the maximum meaningful correlation length), and  $H$  is the Heaviside step function. Although simple, this procedure leads to pronounced artifacts at low- $q$ .

Size effects are at the origin of these artifacts. Salacuse *et al.* [12] identify two types of such effects (see also [26, 27]). First, fixing the total number of particles in the simulation box leads to so-called explicit (or ensemble) size-effects. Second, boundary conditions lead to so-called implicit (or anomalous) size effects. Indeed, boundaries of the simulation box in real space introduce a cut-off which can, if not handled properly, lead in Fourier space to large oscillations and unexpected increase at low- $q$  (see also [28], figure 2a and [29]).

Anomalous size effects are a well known issue within the diffraction community [30], where window functions are widely used as apodizing filters. For peaked spectra, apodizing filters perform very satisfactorily, as the location of each peak is but little affected by the filter. For spectra such as those shown on figures 16 and 19 (with no peaks), the overall shape is significantly modified by the

filter, in a way which is difficult to quantify. Therefore, apodizing filters are not a reliable remedy in the present, general case.

Throughout the years, many methods have been proposed to deal with anomalous size effects [12, 28, 31, 32]. For monodisperse distributions, Salacuse *et al.* [12, 32] introduce the following correction to equation (8b)

$$S(q) = \frac{1}{N} \sum_{\beta, \gamma=1}^N H(r_c - r_{\beta\gamma}) \text{sinc}(qr_{\beta\gamma}) - 3nv_c \frac{j_1(qr_c)}{qr_c}, \quad (9)$$

( $n = N/V$ : number density of particles,  $v_c$ : volume of the sphere with radius  $r_c$ ). This procedure has successfully been used by Moe and Ediger [33], and more recently by Donev *et al.* [34].

The complemented system approach recently proposed by Lajovic *et al.* [29] can be seen as an extension of this procedure to polydisperse systems. It is derived by assuming that all correlations vanish for distances greater than  $r_c$ . More precisely, the unknown value of the pair correlation function  $g_{AB}(r)$  (where  $A$  and  $B$  are two types of atoms) is replaced with 1 for  $r \geq r_c$ . The resulting formula reads

$$I(q) = \frac{1}{V} \sum_{\beta, \gamma=1}^N b_{\beta}(q)b_{\gamma}(q) H(r_c - r_{\beta\gamma}) \text{sinc}(qr_{\beta\gamma}) - 3v_c \frac{j_1(qr_c)}{qr_c} \left[ \frac{1}{V} \sum_{\beta=1}^N b_{\beta}(q) \right]^2, \quad (10)$$

with  $b_{\beta}(q) = \Delta\rho_{\beta}v_{\beta}F_{\beta}(q)$ . It can readily be verified that for monodisperse systems, (10) coincides with (8a) and (9).

In the reciprocal lattice approach, Frenkel *et al.* [31] use an unmodified version of the basic method, but only for selected values of the vector  $\mathbf{q}$ , namely

$$\mathbf{q}_{hkl} = \frac{2\pi}{L} (h\mathbf{e}_1 + k\mathbf{e}_2 + l\mathbf{e}_3).$$

Why such a selection of  $\mathbf{q}$  efficiently removes anomalous size effects is explained by the fact that the form factor of the (cubic) simulation box is null for each  $\mathbf{q}_{hkl}$  (see equation (19), where the unit-cell  $\mathcal{U}$  should be taken as window  $\mathcal{W}$ ).

This procedure is slightly superior to the correction (9) proposed by Salacuse *et al.* [12], as it also applies to polydisperse distributions. However, in the method of Frenkel *et al.* [31], only very few directions of the scattering-vector  $\mathbf{q}$  are sampled at low- $q$ . This affects the accuracy of the subsequent isotropic averaging of  $I(\mathbf{q})$ , and contrived us not to use this method, as we require the computation to be as reliable as possible at low- $q$ .

For the sake of completeness, the method developed by Tomšič *et al.* [28] should be cited. However, the authors agree that with this method, “the numerical suppression of truncation artifacts is found to be less than optimal” [29].

From the above review, it would seem that only the complemented system approach [29] would suit our needs for a method which applies to polydisperse systems, is accurate at small  $q$ , and removes unwanted size effects.

However, it must be pointed out that this approach only addresses anomalous size effects, while ensemble size effects are not considered. Ensemble size effects also result in spurious oscillations at low- $q$ . Averaging the spectra over many configurations usually solves this issue: for example, figure 1 in [29] shows an average over 100 configurations. In many instances, though, only one configuration is available for the computation, and averaging becomes impossible. In the new method we propose in section III, this problem is overcome by the introduction of a window  $\mathcal{W}$ , which effectively samples the unique configuration  $\mathcal{U}$  (see III A).

Moreover, extension of equation (10) to general (not necessarily granular) heterogeneous media (defined by the map  $\mathbf{x} \mapsto \eta(\mathbf{x})$ ) is unclear, while the method proposed in section III applies to any type of microstructures.

To close this review, it should also be noted that all above methods involve double sums, as they are based on the direct computation of the scattering *intensity*. Therefore, the required CPU time grows as  $N^2$  [29, figure 5]. Also, even the slightest update of the system (e.g. moving only one particle) requires a full recomputation.

By contrast, our method is based on the computation of the scattering *amplitude*; only simple sums are involved, and the required CPU time grows as  $N$ . Besides, slight changes of the system are easily accommodated: for example, moving a particle only requires subtraction of its former contribution to the total amplitude, and addition of its new contribution. This simple update procedure is highly desirable in reconstructions where the scattering intensity is used as a constraint (and must therefore be computed at each iteration of the optimization algorithm).

### III. MASTERING FINITE SIZE EFFECTS

In this section, we propose a new method for the computation of the scattering intensity of heterogeneous media. This method explicitly accounts for finite size effects and allows for polydispersity and fine sampling of the directions of  $\mathbf{q}$ . It shares some similarities with the periograms [35] commonly used in signal analysis.

Section III A provides an overview of the method. Section III B discusses the removal of implicit size effects. The proposed method is very general; in sections III C and III D, it is specialized to isotropic and granular media. Then, section III E deals with explicit size effects. Finally, the method is validated in section III F.

#### A. Overview of the method

Instead of considering the simulation box  $\mathcal{U}$  (unit-cell) as a whole, we consider only the matter contained in a

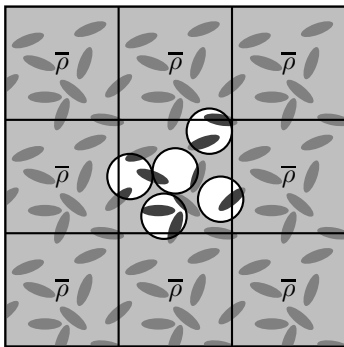


FIG. 2. Illustration of equation (11). Four different locations of the window  $\mathcal{W}$  are considered (white disks). For each of these locations, only that part of the periodic images of a specific particle is considered, which is contained within the window (in dark gray). It is shown in section III B that using  $\eta(\mathbf{x})$  instead of  $\rho(\mathbf{x})$  in (11) is equivalent to replacing the heterogeneous material outside the current window with an average material (homogeneous scattering length density  $\bar{\rho}$ ).

three-dimensional “window”.

More precisely, let  $\mathcal{W} \subset \mathbb{R}^3$  be the so-called window, with characteristic function  $\mathbf{x} \mapsto w(\mathbf{x})$ .  $\mathbf{x} \in \mathcal{U}$  being fixed, we compute the Fourier transform of  $\eta$  inside the window  $\mathcal{W}$  centered at  $\mathbf{x}$

$$A_w(\mathbf{q}, \mathbf{x}) = \int_{\mathbf{y} \in \mathbb{R}^3} w(\mathbf{y} - \mathbf{x}) \eta(\mathbf{y}) \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y}. \quad (11)$$

It should be noticed that the integral in the above equation is computed with periodic boundary conditions. Therefore, intersections of the window  $\mathcal{W}$  with all periodic images of particle  $\beta$  must be considered, and only that part of particle  $\beta$  which is effectively inside  $\mathcal{W}$  is included in the integration process (as illustrated on figure 2). This last point makes the above calculation much more involved than (6), since it precludes the use of closed-form expressions of the form factor  $F_\beta$ .

We then define the intensity  $I_w(\mathbf{q})$  through the following volume average of the local amplitude  $A_w(\mathbf{q}, \mathbf{x})$  over all  $\mathbf{x} \in \mathcal{U}$

$$I_w(\mathbf{q}) = \frac{1}{|\mathcal{W}|} \frac{1}{|\mathcal{U}|} \int_{\mathcal{U}} |A_w(\mathbf{q}, \mathbf{x})|^2 d^3\mathbf{x}, \quad (12)$$

where  $|\mathcal{U}|$  (resp.  $|\mathcal{W}|$ ) denotes the volume of the unit-cell (resp. the window).

The rationale for defining  $I_w(\mathbf{q})$  as a volume average is twofolds. First, the heterogeneous media under consideration are statistically homogeneous. All points  $\mathbf{x}$  being equivalent, there is no reason why the window  $\mathcal{W}$  should be centered at a specific point, and all possible locations should be considered. Second, the scattering intensity pattern is the signature of the fluctuations of the local scattering-length density (for example, the intensity at zero-angle is proportional to the so-called static compressibility of the material [23, section V C]). Fixing the total number of particles in the simulation box effectively kills

these fluctuations for length-scales  $\sim L$ ; this results in ensemble size effects [12]. However, fluctuations at length-scales smaller than  $L$  are not prevented. Using multiple windows  $\mathcal{W}$  captures these fluctuations, and explicitly accounts for ensemble size effects.

Indeed, we prove in appendix A that equation (12) is a biased estimate of the true intensity  $I(\mathbf{q})$ , provided that  $\text{diam } \mathcal{W} < L/2$ . More precisely

$$I_w(\mathbf{q}) = \frac{1}{(2\pi)^3} \int_{\mathbf{p} \in \mathbb{R}^3} \hat{\gamma}_w(\mathbf{q} - \mathbf{p}) I(\mathbf{p}) d^3\mathbf{p}, \quad (13)$$

where  $\gamma_w$  is the normalized correlation function of the window  $\mathcal{W}$  [23], and  $\hat{\gamma}_w$  its Fourier transform (see appendix A, equations (A4) and (A5)). From (13),  $I_w$  appears to be the result of the convolution of the desired spectrum  $I$  with a known kernel; for this reason, it will be called the *blurred intensity*.

It is interesting to note that the convolution product in (13) stems from the fact that (12) is a volume average over all locations of the window  $\mathcal{W}$ . By contrast, only one location of  $\mathcal{W}$  is considered in section II B, with the benefit that a larger window can be used ( $\text{diam } \mathcal{W} < L$  instead of  $\text{diam } \mathcal{W} < L/2$ ); the price to pay is unquantified (ensemble) size effects. One of the main contributions of this paper is the proof that these size effects can be rigorously quantified through equation (13) when multiple smaller windows are used.

In our implementation of the method outlined above, integral (12) is discretized on a regular grid (typically  $8 \times 8 \times 8$ ): the window  $\mathcal{W}$  is centered at each vertex of this grid in turn. For each location of the window, integral (11) is then computed semi-analytically. This leads to an estimate of  $I_w(\mathbf{q})$ . If necessary, sampling over all directions of  $\mathbf{q}$  then provides an estimate of the isotropic average  $I_w(q)$ .

How  $I(\mathbf{q})$  is retrieved from  $I_w(\mathbf{q})$  is detailed in section III E. In section III B, we first discuss the use of  $\eta(\mathbf{x})$  in place of  $\rho(\mathbf{x})$  in equation (11); in sections III C and III D we then go on to show how the previous expressions can be specialized to particulate, statistically isotropic media.

## B. Scattering-length density vs. fluctuations of this density

Attention should be drawn to the fact that in (11),  $A_w(\mathbf{q}, \mathbf{x})$  is defined as the Fourier transform of the fluctuations  $\eta(\mathbf{x})$  of the scattering-length density. This definition is somewhat counter-intuitive, and it would have been more natural to define  $A_w(\mathbf{q}, \mathbf{x})$  as the Fourier transform of the scattering-length density  $\rho(\mathbf{x})$  itself.

While strictly equivalent for very large samples (see the discussion about equations (1) and (3)), these two definitions lead to widely different results in the case of simulation boxes of limited extent. We found that it is essential to use  $\eta(\mathbf{x})$  and not  $\rho(\mathbf{x})$  in (11), as this definition removes most of the implicit size effects induced by the finiteness of the window  $\mathcal{W}$ . This assertion is justified

heuristically below, and a more quantitative illustration can be found in section III F.

We consider a homogeneous system, with uniform scattering length density  $\bar{\rho}$ . Obviously, for such a system

$$I(\mathbf{q}) = 0 \quad \text{and} \quad \eta(\mathbf{x}) = 0,$$

and we find as expected, from (11) and (12)

$$A_w(\mathbf{q}, \mathbf{x}) = 0 \quad \text{and} \quad I_w(\mathbf{q}) = 0.$$

However, if  $A_w(\mathbf{q}, \mathbf{x})$  had been defined as the Fourier transform of the scattering-length density  $\rho(\mathbf{x})$ , instead of its fluctuations  $\eta(\mathbf{x})$ , we would have found

$$A_w(\mathbf{q}, \mathbf{x}) = \bar{\rho} |\mathcal{W}| \exp(-i\mathbf{q} \cdot \mathbf{x}) F_w(q)$$

where  $F_w$  is the form factor of the window  $\mathcal{W}$

$$F_w(q) = \frac{1}{|\mathcal{W}|} \int_{\mathbf{x} \in \mathcal{W}} \exp(-i\mathbf{q} \cdot \mathbf{x}) d^3\mathbf{x}. \quad (14)$$

The resulting scattering spectrum would then have been given by

$$I_w(q) = \bar{\rho}^2 |\mathcal{W}| F_w(q)^2. \quad (15)$$

The above incorrect expression exhibits marked, unwanted oscillations at low- $q$  which are merely the signature of the window  $\mathcal{W}$ , and do not reflect the internal microstructure of the medium contained in  $\mathcal{W}$ . This was already noted by Tomšič *et al.* [28].

The proposed replacement of the scattering length density  $\rho(\mathbf{x})$  with its fluctuations  $\eta(\mathbf{x})$  in (11) is equivalent to embedding the spherical window  $\mathcal{W}$  in a homogeneous, average medium. Indeed, since  $\eta(\mathbf{x}) = \rho(\mathbf{x}) - \bar{\rho}$ , (11) also reads

$$A_w(\mathbf{q}, \mathbf{x}) = \int_{\mathbf{y} \in \mathbb{R}^3} w(\mathbf{y} - \mathbf{x}) \rho(\mathbf{y}) \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y} \\ - \int_{\mathbf{y} \in \mathbb{R}^3} w(\mathbf{y} - \mathbf{x}) \bar{\rho} \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y}.$$

From Babinet's principle,  $w(\mathbf{y} - \mathbf{x})$  in the second integral can be replaced (up to a Dirac generalized function) with  $-[1 - w(\mathbf{y} - \mathbf{x})]$

$$A_w(\mathbf{q}, \mathbf{x}) = \int_{\mathbf{y} \in \mathbb{R}^3} w(\mathbf{y} - \mathbf{x}) \rho(\mathbf{y}) \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y} \\ + \int_{\mathbf{y} \in \mathbb{R}^3} [1 - w(\mathbf{y} - \mathbf{x})] \bar{\rho} \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y}.$$

The quantity in square brackets  $[1 - w(\mathbf{y} - \mathbf{x})]$  is non-zero only for points outside the window  $\mathcal{W}$ . Therefore, the second term can be understood as the contribution to the total scattered amplitude of the exterior domain, filled with a homogeneous, average material.

To close this section, it should be noted that Lajovic *et al.* [29] also claim that the complemented system approach (see equation (10) in the present paper) is equivalent to “complementing the missing surroundings of

each particle with an average image of the system”. In their work however, the physical properties of this “average” material are unclear, while in the present paper, the uniform scattering length density of the outside material is clearly the volume average  $\bar{\rho}$ .

### C. Isotropic average of the blurred spectrum

In real small-angle scattering experiments, the measured scattering intensity  $I(q)$  is usually the isotropic average of the intensity  $I(\mathbf{q})$  defined in (2) (with  $q = |\mathbf{q}|$ ). Comparing computational to experimental results therefore requires the computation of the following isotropic average

$$I_w(q) = \frac{1}{4\pi} \int_{|\mathbf{n}|=1} I_w(q\mathbf{n}) d^2\mathbf{n}. \quad (16)$$

Although not mandatory, selection of a spherical window  $\mathcal{W}$  is then natural, since such a choice means that no specific direction is preferred throughout the computation. For this particular choice of the window  $\mathcal{W}$ , the following integral relationship can be derived from (13) (see the proof in appendix B)

$$qI_w(q) = \frac{6R}{\pi} \int_0^{+\infty} \{\varphi[2R(q-p)] - \varphi[2R(q+p)]\} \\ \times pI(p) dp, \quad (17)$$

where  $I(q)$  (resp.  $I_w(q)$ ) is the isotropic average of the true (resp. blurred) spectrum,  $R$  is the radius of the spherical window  $\mathcal{W}$ , and the kernel  $\varphi$  is given by

$$\varphi(t) = \frac{1}{t^4} \left( 1 + \frac{t^2}{2} - \cos t - t \sin t \right). \quad (18)$$

The occurrence in equation (17) of the length-scale  $R$  shows that size effects are explicitly accounted for in the present method. It should be emphasized that (17) is rigorous. In other words, similarly to all other existing methods for computing the scattering intensity, ours is not devoid of size effects. However, contrary to all other existing methods, we *know* precisely what these effects are.

To close this section, it is reminded that the diameter of the window must not be larger than half the size of the unit-cell. In other words, we must have in the present case  $R < L/4$ . This condition ensures that no particle is correlated with one of its own periodic images. All computations presented in this work were carried out with spherical windows, with maximum allowable size  $R = \text{diam } \mathcal{W}/2 = L/4$ .

### D. Specialization of the method to granular media

The method introduced in the present work is general, as it requires only the local map  $\mathbf{x} \mapsto \eta(\mathbf{x})$ . However, the

general equation (11) can be specialized to particulate media, for which it is convenient to introduce the contrast in scattering length density

$$A_w(\mathbf{q}, \mathbf{x}) = \sum_{\beta=1}^N \Delta\rho_\beta \int_{\mathbf{y} \in \omega_\beta} w(\mathbf{y} - \mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y} - \Delta\bar{\rho} |\mathcal{W}| \exp(-i\mathbf{q} \cdot \mathbf{x}) F_w(\mathbf{q}), \quad (19)$$

where the notations introduced in section II have been adopted,  $\omega_\beta$  is the domain occupied by particle  $\beta$  and its periodic images and  $F_w$  is given by (14).  $\Delta\bar{\rho}$  denotes the volume average of  $\Delta\rho$  on the *entire* simulation box

$$\Delta\bar{\rho} = \sum_{\beta=1}^N \frac{v_\beta}{|\mathcal{U}|} \Delta\rho_\beta.$$

If particle  $\beta$  is completely included in the window  $\mathcal{W}$  (centered at  $\mathbf{x}$ ), then the integral in (19) reduces to  $v_\beta F_\beta(\mathbf{q})$ , closed-form expressions of which exist for many particle shapes (see equation (7) for spherical particles). For the particles which cross the boundary of the window, this integral must generally be computed numerically. Efficient techniques can be implemented for spherical particles, see appendix C.

### E. Deconvolution of the blurred spectrum

It must be emphasized again that the method introduced in section III A does not provide a direct estimate of the true scattering intensity  $I(\mathbf{q})$ . Indeed, the blurred spectrum  $I_w(\mathbf{q})$  is the result of the convolution of the true spectrum  $I(\mathbf{q})$  with a known kernel, see equation (13). The purpose of this section is to show how  $I(\mathbf{q})$  can be retrieved from the computed  $I_w(\mathbf{q})$ .

In the remainder of this paper, we will assume that the window  $\mathcal{W}$  used to compute the blurred spectrum  $I_w(\mathbf{q})$  is spherical. Also, we will concentrate on the determination of the isotropic average  $I(q)$  from the isotropic average of  $I_w(q)$  via identity (17).

The mathematical analysis of this identity is greatly simplified if  $q \mapsto I(q)$  is first symmetrized about the origin. In what follows, we will therefore adopt the convention  $I(q) = I(-q)$ ,  $q < 0$ . Introducing

$$J(q) = qI(q) \quad \text{and} \quad J_w(q) = qI_w(q), \quad (20)$$

equation (17) then reduces to a simple convolution product

$$J_w(q) = \int_{-\infty}^{+\infty} k(q-p)J(p)dp, \quad \text{with } k(q) = \frac{6R}{\pi} \varphi(2Rq),$$

or, in a more compact form ('\*' denoting convolution product)

$$J_w(q) = (k * J)(q). \quad (21)$$

Taking the Fourier transform of both sides, we then find

$$\hat{J}_w(x) = \hat{k}(x)\hat{J}(x), \quad (22)$$

with

$$\hat{J}(x) = \int_{-\infty}^{+\infty} J(q) \exp(-iqx) dx,$$

and similar relations for  $\hat{J}_w$  and  $\hat{k}$ . From equation (22) it would seem that retrieving  $I$  (the quantity of interest) from  $I_w$  (the quantity effectively computed) reduces to a straightforward division in Fourier space. In fact, the situation is more complex, since  $\hat{k}(x) = 0$  for  $|x| > 2R$  (see equations (D1) and (D2) in appendix D). Therefore, the high- $x$  values of  $\hat{J}$  cannot be retrieved from the calculation presented here; this is consistent with the fact that we are working on a finite size simulation (where large correlation lengths cannot be reached).

To sum up, inverting (17) is not possible because we are missing information at high- $x$ , and (17) admits multiple solutions. To compensate for this missing information, we must introduce some prior knowledge about  $I(q)$ , in order to select a reasonable solution for  $I(q)$ . In mathematical terms, this is known as regularization. In the present work, we used standard Tikhonov regularization (see e.g. [36]), combined with the discrepancy principle. The overall procedure is detailed in the remainder of this section.

We first note from (22) that  $J_w(q)$  is band-limited, which has deep implications on the sampling of  $J_w(q)$  as well as the calculation of its Fourier transform.

The Shannon-Nyquist theorem indeed states that the band-limited function  $J_w$  can be fully reconstructed from its sampling at evenly spaced values  $q_m = m\pi/(2R)$  ( $m \in \mathbb{Z}$ )

$$\begin{aligned} J_w(q) &= \sum_{m=-\infty}^{+\infty} J_w\left(\frac{m\pi}{2R}\right) \text{sinc}(2Rq - m\pi), \\ &= \sum_{m=1}^{+\infty} 2m\pi(-1)^m J_w\left(\frac{m\pi}{2R}\right) \frac{\sin(2Rq)}{(2Rq)^2 - (m\pi)^2}, \end{aligned} \quad (23)$$

where the second equality accounts for  $J_w$  being an odd function.

Equation (23) is essential from the practical point of view, since it indicates how the blurred spectrum should be reliably sampled. In the present work, the  $M$  first values of  $I_w$  were first sampled at the required spacing. Multiplication by the corresponding value of  $q$  then provided the finite series

$$J_w(0), J_w\left(\frac{\pi}{2R}\right), \dots, J_w\left[\frac{(M-1)\pi}{2R}\right],$$

from which  $J_w$  was fully reconstructed by means of the interpolation formula (24), where the infinite sum was truncated at  $m = M$ . Such a truncation is meaningful (provided  $M$  is large enough), since  $q^4 I_w(q) \rightarrow \text{Const.}$  as



$q \rightarrow +\infty$  (Porod regime), therefore  $q^3 J_w(q) \rightarrow \text{Const.}$  as  $q \rightarrow +\infty$ .

Another implication of the Shannon-Nyquist theorem is the possibility to compute *exactly* the Fourier transform of  $J_w$  from its sampled values. Indeed, from the known Fourier transform of the sine cardinal function, combined with (23), we find

$$\begin{aligned} \hat{J}_w(x) &= \frac{\pi}{2R} \text{rect}\left(\frac{x}{2R}\right) \sum_{m=-\infty}^{+\infty} J_w\left(\frac{m\pi}{2R}\right) \exp\left(-i\frac{m\pi x}{2R}\right), \\ &= -\frac{i\pi}{R} \text{rect}\left(\frac{x}{2R}\right) \sum_{m=1}^{+\infty} J_w\left(\frac{m\pi}{2R}\right) \sin\left(\frac{m\pi x}{2R}\right), \end{aligned} \quad (25)$$

where the second line again results from  $J_w$  being odd, and

$$\text{rect}(\omega) = \begin{cases} 1 & \text{if } |\omega| < 1, \\ 0 & \text{otherwise.} \end{cases}$$

Truncating the sum in (25) leads to the approximate formula for  $x = 2Rk/M$  ( $k = 0, \dots, M-1$ )

$$\hat{J}_w\left(\frac{2Rk}{M}\right) \simeq -\frac{i\pi}{R} \sum_{m=0}^{M-1} J_w\left(\frac{m\pi}{2R}\right) \sin\left(\frac{\pi mk}{M}\right). \quad (26)$$

The above expression can be recognized as the discrete sine transform of the finite data series  $J_w(0), \dots, J_w[(M-1)\pi/(2R)]$ . Furthermore, the  $J_w[m\pi/(2R)]$  (therefore, the *full* description of  $J_w$ ) can be retrieved from the  $\hat{J}_w(2Rk/M)$  by inverse discrete sine transform

$$J_w\left(\frac{m\pi}{2R}\right) \simeq \frac{2iR}{M\pi} \sum_{k=0}^{M-1} \hat{J}_w\left(\frac{2Rk}{M}\right) \sin\left(\frac{\pi mk}{M}\right). \quad (27)$$

Both direct and inverse discrete sine transforms are computed by means of the fast sine transform.

With these preliminary results at hand, it is now possible to introduce the procedure we used to perform the deconvolution of equation (17). As already stated, additional constraints (prior knowledge) must be imposed to the solution to be selected, for inversion of problem (17) to be possible. One such additional constraint is to search for a band-limited solution  $J$ . This is a reasonable assumption, since neglecting high correlation lengths leads to a smoother solution; besides, equation (22) shows that high correlation length modes of  $J$  cannot be retrieved from  $J_w$  (some data is lost through the convolution product (21)).

In theory, requiring  $J(q)$  to be band-limited makes it uniquely determined, since its Fourier transform is given by

$$\hat{J}(x) = \begin{cases} \frac{\hat{J}_w(x)}{\hat{k}(x)} & \text{if } |x| < 2R, \\ 0 & \text{otherwise.} \end{cases}$$

In practice however, this constraint is not sufficient. Indeed, division by  $\hat{k}$  tends to amplify high correlation length modes of  $J_w$  (since  $\hat{k}(x) \rightarrow 0$  as  $|x| \rightarrow 2R$ ). These modes are corrupted by numerical noise, which results in spurious oscillations of  $J(q)$  (particularly at low- $q$ ).

In the present work, Tikhonov regularization was used in order to dampen these oscillations. A full description of this widely used technique is beyond the scope of this paper (see for example [36] and references therein). Suffice it to say that in this approach,  $J$  is defined as the minimizer of the following functional

$$\|k * J - J_w\|_2^2 + \lambda^2 \|J\|_2^2, \quad (28)$$

rather than the exact solution of equation (21). More details on the selection of the user-specified regularization parameter  $\lambda$  are provided below.

The solution to the above optimization problem is explicit in Fourier space. Indeed, Parseval's identity shows that minimizing (28) is equivalent to minimizing

$$\begin{aligned} \|\hat{k}\hat{J} - \hat{J}_w\|_2^2 + \lambda^2 \|\hat{J}\|_2^2 &= \int_{-\infty}^{+\infty} \left[ \hat{k}(x)\hat{J}(x) - \hat{J}_w(x) \right]^2 dx \\ &\quad + \lambda^2 \int_{-\infty}^{+\infty} \hat{J}(x)^2 dx. \end{aligned}$$

The first variation of this functional with respect to  $\hat{J}$  reads

$$2 \int_{-\infty}^{+\infty} \left\{ [\hat{k}(x)^2 + \lambda^2] \hat{J}(x) - \hat{k}(x)\hat{J}_w(x) \right\} \delta \hat{J}(x) dx,$$

which must be null for any variation  $\delta \hat{J}$  of  $\hat{J}$ . The regularized solution (in the sense of Tikhonov) therefore reads in Fourier space

$$\hat{J}(x) = \frac{\hat{k}(x)}{\hat{k}(x)^2 + \lambda^2} \hat{J}_w(x), \quad (29)$$

which shows that  $J$ , like  $J_w$ , is band-limited in this approach. Therefore, the Shannon-Nyquist theorem also applies to the reconstructed  $J(q)$ . In other words, equations (23), (25), (26) and (27) remain valid if  $J$  is substituted to  $J_w$ , and the whole deconvolution procedure can be summarized as follows

1. Compute  $I_w[m\pi/(2R)]$  for  $m = 0, \dots, M-1$  using (11) and (12), or (19) and (12).
2. Compute  $J_w[m\pi/(2R)]$  for  $m = 0, \dots, M-1$  using (20).
3. Compute  $\hat{J}_w(2Rk/M)$  for  $k = 0, \dots, M-1$  using (26).
4. Compute  $\hat{J}(2Rk/M)$  for  $k = 0, \dots, M-1$  using (29).
5. Compute  $J[m\pi/(2R)]$  for  $m = 0, \dots, M-1$  using (27) (where  $J$  should be substituted to  $J_w$ ).

6. Interpolate  $J(q)$  for any  $0 \leq q \leq (M-1)\pi/(2R)$  using (24) (again,  $J$  should be substituted to  $J_w$ ).
7. Use (20) to retrieve  $I(q)$  for any  $0 \leq q \leq (M-1)\pi/(2R)$ .

It is interesting to note that the above deconvolution procedure is based on assumptions similar to the complemented system approach of Lajovic *et al.* [29]. Indeed, reconstructing  $J(q)$  as a band-limited signal means that two-point correlations are neglected for  $r \geq 2R$ . However, unlike the complemented system approach, correlations are brought smoothly down to zero (see (29)), through multiplication by  $\hat{k}(x)/[\hat{k}(x)^2 + \lambda^2]$ , which can be seen as a specially designed apodization filter.

The above procedure requires the selection of a specific value for the regularization parameter  $\lambda$ . Obviously, this should be done as objectively as possible.

Many criteria have been proposed in the past for an objective selection of  $\lambda$  (see e.g. [37]); the most frequently used are probably the L-curve criterion [38, 39] or the generalized cross-validation criterion [40]. Unfortunately, none of these criteria proved satisfactory for the present application. We therefore resorted to the discrepancy principle [41], which proved more robust, but required quantification of the noise level in the input data  $I_w[m\pi/(2R)]$ .

The discrepancy principle is based on the fact that selecting the regularization parameter  $\lambda$  results from a compromise between fidelity (achieved with small values of  $\lambda$ ) and smoothness (achieved with large values of  $\lambda$ ) of the reconstructed solution.

In Morozov's view, the largest value of  $\lambda$  achieving the required fidelity of the reconstructed solution must be selected. Fidelity of the solution is assessed by comparison of the residual with the experimental noise; it is required that the former must be lower than the latter.

In the present work, four configurations were considered for each value of the polydispersity index  $\alpha$  (which will be defined more precisely in section IV A). An estimate of the statistical noise is therefore given by the point-wise standard deviation of the four resulting spectra. Then, the residual is the difference between the initial (blurred) spectrum  $I_w(q)$  and the "reblurred" spectrum

$$\frac{(k * J)(q)}{q},$$

where  $J$  is the reconstructed solution. The discrepancy principle results in the following simple procedure:  $\lambda$  is progressively increased until the reblurred spectrum is no longer contained within the error-bars drawn around  $I_w$ .

## F. Validation of the method

The method proposed above must be validated against reference data. To the best of our knowledge, exact expressions of the scattering pattern are not available, even

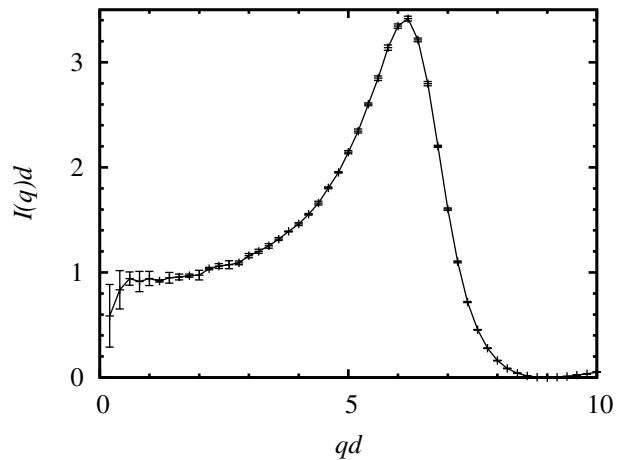


FIG. 3. The average reference spectrum  $I_{\text{ref}}(q)$  of the large ( $N = 108000$ ) configurations of equilibrium monodisperse hard spheres. Due to the size of the configurations considered here, the resulting curve is relatively smooth, even at small  $q$ . In figures 3 to 8, both  $q$  and  $I(q)$  have been made dimensionless through multiplication by the diameter  $d$  of the particles; furthermore,  $\Delta\rho = 100d^{-2}$ .

for very simple granular systems. In the present paper, reference scattering patterns are therefore *computed* on systems of monodisperse hard spheres, using the method of Salacuse *et al.* [12]. The computation is carried out on large configurations in order to minimize finite-size effects.

Using a standard Monte-Carlo procedure [42], we therefore generated two sets of four configurations. So-called large (resp. small) configurations contain  $N = 108000$  (resp.  $N = 4000$ ) particles; the volume fraction of the particles is set to  $f = 0.4$  in both families of configurations.

The method of Salacuse *et al.* [12] was applied to the large ( $N = 108000$  particles) configurations in order to compute the average reference spectrum  $I_{\text{ref}}(q)$  shown in figure 3, where it is observed that small- $q$  oscillations are kept to a minimum due to the size of the configurations.

The new procedure described above (see sections III A to III D) was then applied to the small ( $N = 4000$  particles) configurations to compute the isotropically averaged blurred spectrum  $I_w(q)$ . Generating four different configurations allowed us to estimate the numerical noise on  $I_w(q)$ , which was required for a reliable estimation of the regularization parameter  $\lambda$  through the discrepancy principle. The resulting average blurred spectrum is shown in figure 4. As expected, the error-bars are slightly larger in the low- $q$  region (which corresponds to large correlation lengths).

The deblurred spectrum is then derived from the procedure described in section III E. The resulting curves are shown in figures 5 (linear scale) and 6 (logarithmic scale), where they are compared with the reference spectrum  $I_{\text{ref}}(q)$ . It is apparent on figure 5 that the location of the first peak is well captured, while its height is slightly

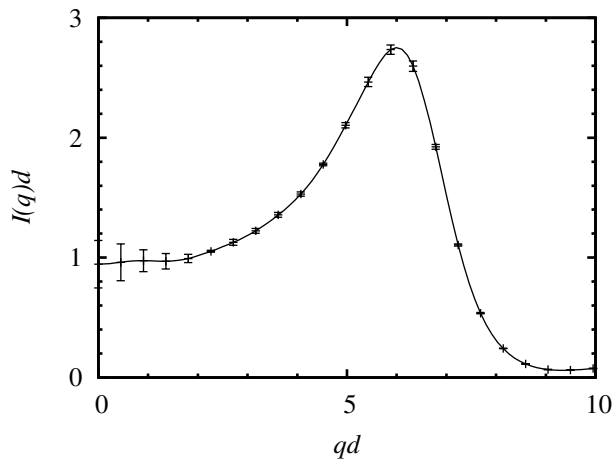


FIG. 4. The average blurred spectrum  $I_w(q)$  of the small ( $N = 4000$  particles) configurations of equilibrium monodisperse hard spheres.

underestimated. This was to be expected from the regularization procedure used here (the discrepancy principle is known to overestimate the regularization parameter  $\lambda$ ). Nevertheless, the overall agreement between actual and expected spectra is very satisfactory. Figure 6 further confirms this observation, since representation in logarithmic scale shows that the location of the zeros of the spectrum is also captured very accurately.

This application also shows that the method of Salacuse *et al.* [12] is more susceptible to unphysical oscillations at low- $q$  than our method. Indeed, computations carried out with this method on small configurations ( $N = 4000$  particles) are shown in figure 1 (curve b), and should be compared with computations carried out with our method on the same configurations (see figure 5, curve b), the latter being less oscillatory at low- $q$ . It seems that this sensitivity to size effects increases with the compacity of the system, as will be illustrated in section IV B (figure 12).

To close this section, we again emphasize how important it is to use the fluctuations  $\eta(\mathbf{x})$  instead of the scattering-length density  $\rho(\mathbf{x})$  (or equivalently the contrast  $\Delta\rho(\mathbf{x})$ ) in formula (11).

This is best demonstrated by performing the same calculation as above, substituting  $\rho(\mathbf{x})$  to  $\eta(\mathbf{x})$  (deblurring was not performed, as it was not necessary to make our point). The resulting blurred spectrum is shown in figures 7 and 8. At low- $q$ , the spectrum is dominated by spurious oscillations (see figure 7). Figure 8 shows that these oscillations are in fact the contribution of the squared form factor of the window  $\mathcal{W}$  (see also equation (15))

$$\bar{\rho}^2 |\mathcal{W}| F_w(q)^2, \quad (30)$$

It is clear from figure 7 that  $\eta(\mathbf{x})$  should indeed be preferred over  $\rho(\mathbf{x})$  for the computation of the scattering intensity.

This first example confirms the validity of the proposed

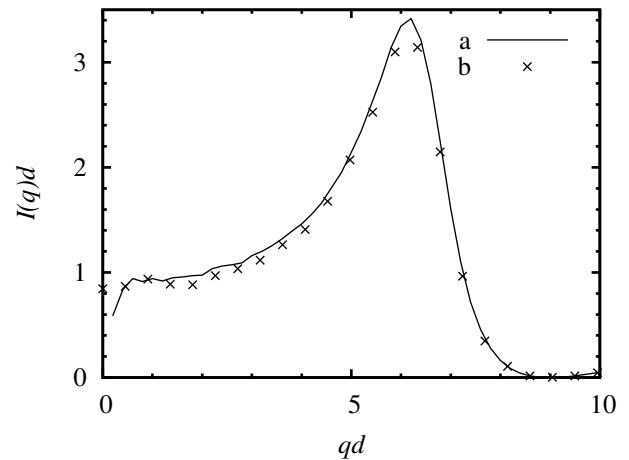


FIG. 5. The reference spectrum  $I_{\text{ref}}(q)$  (a), and the deblurred spectrum  $I(q)$  (b), derived from  $I_w(q)$  shown in figure 4; the agreement is very satisfactory.

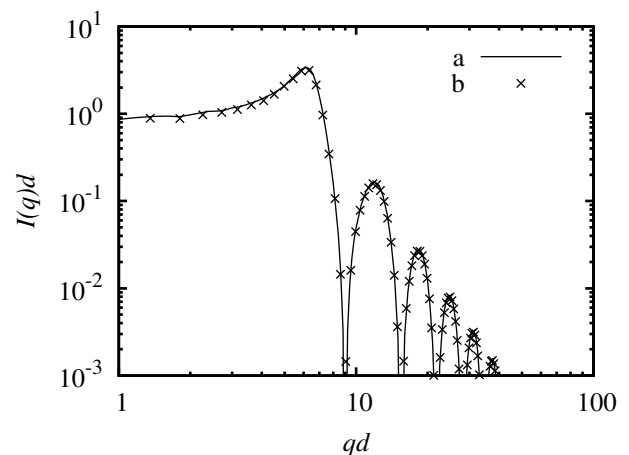


FIG. 6. Same as figure 5, in logarithmic scale.

method, which is applied in section IV to configurations for which the true scattering intensity is not known.

#### IV. APPLICATION TO POLYDISPERSE GRANULAR MEDIA

The present section addresses the generation of assemblies of spherical particles with various indices of polydispersity, and low porosity (below 35%). A special procedure is required for the generation of such compact configurations. This procedure is described in section IV A, and applied to the generation of twenty compact polydisperse configurations of hard spheres.

In section IV B, the scattering intensity of each of these configurations is computed; the resulting curves are then analyzed.

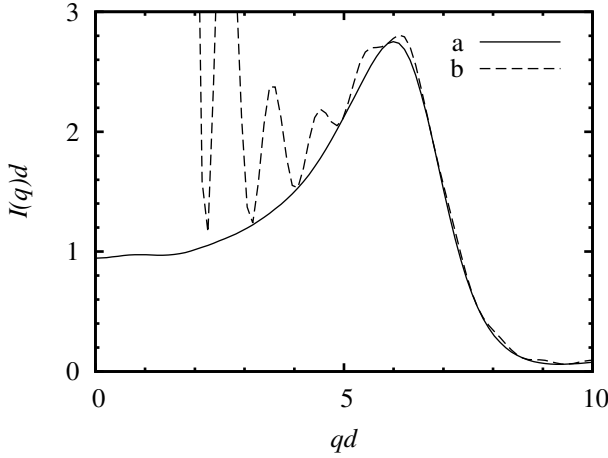


FIG. 7. The average blurred spectrum  $I_w(q)$  of the small ( $N = 4000$  particles) configurations of equilibrium monodisperse hard spheres, computed with formula (11) (a), and a modified version of this formula, where  $\Delta\rho(\mathbf{x})$  was substituted to  $\eta(\mathbf{x})$  (b). The second calculation exhibits spurious oscillations at low- $q$ .

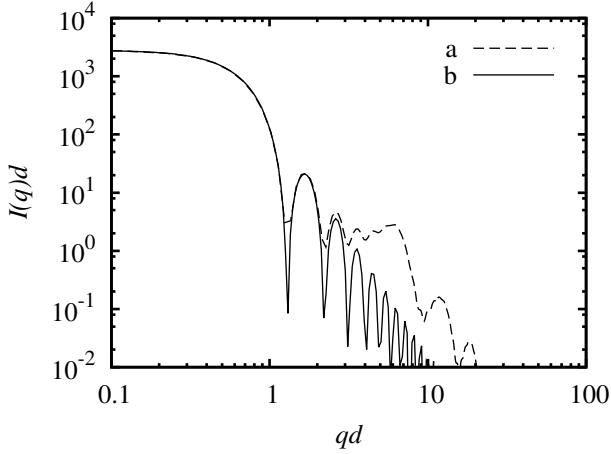


FIG. 8. The average blurred spectrum  $I_w(q)$  of the small ( $N = 4000$  particles) configurations of equilibrium monodisperse hard spheres (a), and the squared form factor of the spherical window, given by equation (30) (b). Unlike the curve shown in figure 4,  $\Delta\rho(\mathbf{x})$  was substituted to  $\eta(\mathbf{x})$  in formula (11). The squared form factor of the window dominates the computed spectrum at low- $q$ , leading to an incorrect result.

### A. Generation of dense packings of particles

For all assemblies of spheres considered in the present work, the target compacity is fixed at 63.75 % and 64 % for mono- and polydisperse configurations respectively; it is therefore comparable to experimentally measured compacities in real cement pastes, while remaining below the so-called random close packing density of monodisperse spherical particles.

Generating assemblies of hard particles near the random close packing density is a difficult task. Most algorithms

are based on a molecular dynamics approach, in two [43] and three [44] dimensions. The basic idea is to start from a loose packing, which is densified as the simulation proceeds, either by reducing the volume of the simulation box [43–45], or by increasing the size of the particles [46]. This approach is rather effective and flexible; it has been extended to polydisperse assemblies [47], and assemblies of anisotropic particles (e.g. ellipsoids) [48, 49]. The downside is the relatively high degree of complexity of these so-called event-driven algorithms.

Though less general, the alternative approach adopted in the present paper leads to very simple numerical codes, while running in a reasonable time. Rather than a molecular dynamics simulation, we carried out a Monte-Carlo simulation of an assembly of (possibly polydisperse) spheres in the minimum image convention, aiming at the minimization of the following (non-physical) “energy”

$$E = \sum_{1 \leq \beta \neq \gamma \leq N} \max\left(\lambda_{\beta\gamma}^{-1} - 1, 0\right), \quad (31)$$

where  $\lambda_{\beta\gamma}$  denotes the common scaling factor to be applied simultaneously to both particles  $\beta$  and  $\gamma$  to bring them into (external) contact. If the configuration is admissible, then there is no overlap, and  $\lambda_{\beta\gamma} \geq 1$ , so that the above energy  $E$  is rigorously 0.

The simulation is started with a non-admissible configuration, in which the particles are placed randomly (with many overlaps): the initial energy is non-zero. During one cycle of the simulation, each particle in turn is submitted to a random translation, the magnitude of which is controlled by the user. Following the standard Metropolis approach [42, 50], the proposed move is accepted with probability

$$\min[\exp(-\beta\Delta E), 1],$$

where  $\Delta E$  denotes the change in energy incurred by the move under consideration. For physically meaningful energies,  $\beta$  is related to the temperature of the system; in the present case, it has no physical meaning.

In view of minimizing the cost function  $E$  given by (31) using a simulated annealing strategy [51], the  $\beta$ -factor is gradually increased, following the “cooling” schedule

$$\beta' = (1 + \epsilon)\beta \quad (32)$$

where  $\epsilon > 0$  (typically  $\epsilon$  ranges from 0.001 to 0.1), and  $\beta'$  is the new value of the  $\beta$ -factor, which is updated every few (typically 4) cycles. It is recalled that, following the terminology of Allen and Tildesley [42], a cycle is completed when each single particle in turn has been submitted to a trial move (both accepted and rejected trials are taken into account in this definition).

The simulation is stopped when the minimum  $E = 0$  is reached. It should be noted that the algorithm might fail to converge if the system gets frozen in a local minimum of the energy  $E$ ; in this case, the simulation is started anew. In order to minimize the number of

Step #	$a$	$f$	$\epsilon$	$\mathcal{N}$
1	0.5	0.58	0.01	4082
2	0.51	0.6155	0.005	9269
3	0.5125	0.6246	0.002	18069
4	0.516	0.6375	0.001	44771

TABLE I. Generation in four steps of a compact assembly of monodisperse hard spheres. The total number of particles is  $N = 4096$ , and the final compacity is  $f = 0.6375$ . In the above table,  $a$  denotes the particle radius in the current step,  $f$  is the effective packing at the end of the current step,  $\epsilon$  is the numerical parameter governing the cooling schedule (32), and  $\mathcal{N}$  is the total number of Monte-Carlo cycles in the current step.

occurrences of this situation, very dense configurations are obtained in several steps. A first (not too dense) configuration is generated following the above procedure. Then each particle in this first configuration is scaled by the same factor; this effectively increases the compacity of the assembly of particles, but also generates overlaps. Simulated annealing is again invoked to correct these overlaps, resulting in a second (admissible) configuration. The procedure is repeated until the desired compacity is reached. Table I shows an example of this procedure, for the generation of an assembly of 4096 monodisperse hard-spheres; four steps (in other words, four successive Monte-Carlo simulations) were necessary in this case to reach the desired compacity  $f = 0.6375$ .

It should be noted that the above procedure is not restricted to spheres. Indeed, it applies to other particle shapes as well, provided that the scaling factor  $\lambda_{\beta\gamma}$  can be computed. In the case of ellipsoids, this quantity is in fact a direct output of the robust overlap criterion derived by Perram and Wertheim [52]. Combined with our Monte-Carlo procedure, this criterion allowed the successful generation of compact assemblies of spheroids, an example of which is shown on figure 9.

This procedure has been used to generate twenty configurations with increasing polydispersity. Their characteristics are gathered in table II, where  $N$  is the number of globules,  $L$  is the size of the (cubic) simulation box,  $f$  is the volume fraction of the globules and  $\alpha$  is the polydispersity index, defined as

$$\alpha = \frac{\sqrt{\langle a^2 \rangle - \langle a \rangle^2}}{\langle a \rangle}, \quad \langle a \rangle = \frac{1}{N} \sum_{\beta=1}^N a_{\beta}, \quad \langle a^2 \rangle = \frac{1}{N} \sum_{\beta=1}^N a_{\beta}^2.$$

As shown in table II, configurations **monoxxx** are monodisperse (why we considered larger monodisperse configurations, namely **mono020**, **mono024**, **mono028** and **mono032** will be explained in section IV B below), while all other configurations are log-normally distributed. After generation, each configuration is scaled so as to ensure that the (number-weighted) average radius  $\langle a \rangle$  of the globules is 2.5 nm.

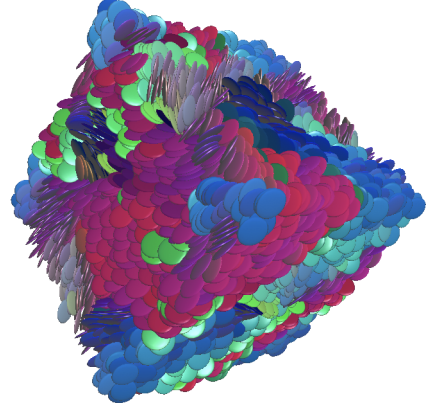


FIG. 9. An example of dense packing of oblate spheroids generated following the procedure described in section IV A. The radii of the particles are  $a = 200$  (equatorial radius),  $c = 25$  (polar radius). The total number of particles is  $N = 10000$ , the compacity is 60 %. [Color online] Each particle is colored according to its orientation, which emphasizes the fact that high compacity causes local orientational order.

Name	$N$	$L$ [nm]	$f$	$\alpha$
<b>mono004</b>	4096	75	0.6375	0
<b>mono008</b>	4096	75	0.6375	0
<b>mono012</b>	4096	75	0.6375	0
<b>mono016</b>	4096	75	0.6375	0
<b>mono020</b>	32768	150	0.6375	0
<b>mono024</b>	32768	150	0.6375	0
<b>mono028</b>	32768	150	0.6375	0
<b>mono032</b>	32768	150	0.6375	0
<b>poly006</b>	4097	78	0.64	0.20
<b>poly012</b>	4097	78	0.64	0.20
<b>poly018</b>	4097	78	0.64	0.20
<b>poly024</b>	4097	78	0.64	0.20
<b>poly030</b>	4094	94	0.64	0.51
<b>poly036</b>	4094	94	0.64	0.51
<b>poly042</b>	4094	94	0.64	0.51
<b>poly048</b>	4094	94	0.64	0.51
<b>poly051</b>	4093	115	0.64	0.78
<b>poly054</b>	4093	115	0.64	0.78
<b>poly057</b>	4093	115	0.64	0.78
<b>poly060</b>	4093	115	0.64	0.78

TABLE II. characteristics of the configurations considered in this paper.

## B. Results and discussion

For each value of the polydispersity index  $\alpha$ , four configurations were generated. Then, the four (blurred) small-angle scattering spectra were computed according to the procedure described in section III. The average of these four spectra is plotted in figures 10 (monodisperse config-

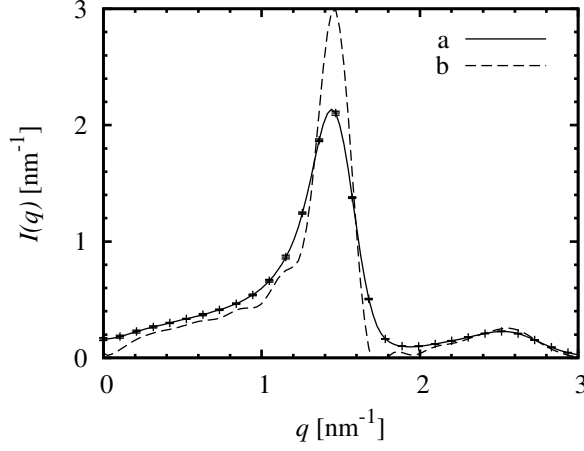


FIG. 10. The average blurred spectrum  $I_w(q)$  (a) of configurations `mono004`, `mono008`, `mono012`, `mono016`, and the resulting deblurred spectrum  $I(q)$  (b). In order to allow for the direct comparison of various computations, the scattering intensity is shown in absolute scale in figures 10, 11 and 12, with  $\Delta\rho = 1 \text{ nm}^{-2}$ .

urations), 13, 14 and 15 (polydisperse configurations). In order to allow for the direct comparison of various computations, the scattering intensity is shown in absolute scale in figures 10, 11 and 12, with  $\Delta\rho = 1 \text{ nm}^{-2}$ . In figures 13, 14 and 15, arbitrary units are used.

The motivation for averaging four spectra for each value of  $\alpha$  is twofolds. First, it reduces the statistical noise coming from the insufficient sampling in configurational space. Second, it provides an estimate of this statistical noise (through the point-wise standard deviation of these four spectra). This is represented as error-bars in figures 10, 13, 14 and 15, and can further be fed into our deconvolution procedure, in order to find the most appropriate value of the regularization parameter  $\lambda$  (see section III E).

The corresponding “deblurred” spectra  $I(q)$  are superimposed with their “blurred” counterpart  $I_w(q)$  in figures 10, 13, 14 and 15. Besides, all deblurred spectra are gathered in logarithmic scale in figure 17.

We first concentrate on the monodisperse configurations, `mono004`, `mono008`, `mono012` and `mono016`, whose average scattering pattern (see figure 10) exhibits a sharp peak. This indicates pseudo-periodicity in the real space, which was to be expected, as the unique diameter  $d = 5 \text{ nm}$  of the particles constitutes such a pseudo-period ( $d$  is also the minimum center-to-center distance). Interestingly however, our calculation shows that the actual location of the peak ( $q_{\text{peak}} \simeq 1.47 \text{ nm}^{-1}$ ) is greater than  $2\pi/d = 1.25 \text{ nm}^{-1}$ , in good agreement with results published elsewhere [34].

Another remarkable feature of figure 10 is the behavior of  $I(q)$  as  $q \rightarrow 0$ . Indeed, it seems that  $I(0) \simeq 0$ . In order to confirm this result, the same computation was carried out on simulation boxes twice as large (configurations `mono020`, `mono024`, `mono028` and `mono030`, see table II). The resulting deblurred spectrum, is shown in figure 11,

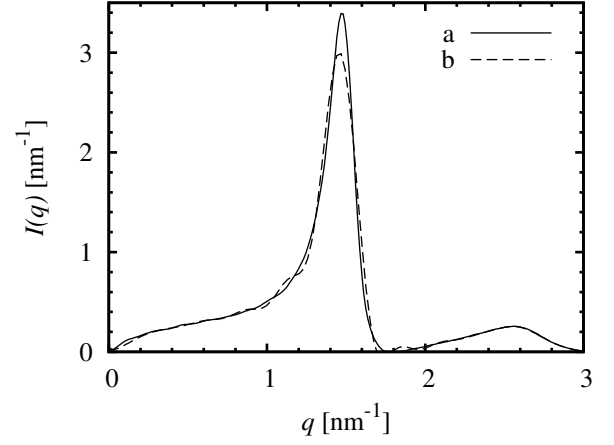


FIG. 11. The deblurred spectrum  $I(q)$  of the monodisperse configurations `mono020`, `mono024`, `mono028` and `mono030` (a), and `mono004`, `mono008`, `mono012`, `mono016` (b). The two graphs are very similar; the location of the peak is identical, while its height is slightly underestimated by the computation on the smaller configurations. This is consistent with the observations made in section III F, and confirms the reliability of the proposed method.

where it is again observed that  $I(0) \simeq 0$ . This result should therefore not be considered as a size-effect, but as a general feature of systems approaching the random close-packing density, which are almost incompressible. It should be noted that the same observation was made by Donev *et al.* [34] using different numerical means, with much larger assemblies of spheres (more than a million particles); this confirms the robustness of the method presented in section III.

To close our analysis of the monodisperse configurations, figure 12 shows a comparison between two procedures for the computation of the scattering intensity. Curve (a) results from the application of our procedure, while curve (b) results from the application of the procedure proposed by Salacuse *et al.* [12, 32]. In both cases, the corrections for anomalous size effects are similar. Therefore, the oscillations observed in (b) should be attributed to ensemble size effects. Indeed, only four configurations are considered for this computation, which is clearly insufficient in the approach of Salacuse *et al.*. These oscillations are not observed in (a), because sampling is widened in this case by the introduction of several windows. Due to the fact that the *same* configuration may be observed multiple times (albeit through different windows), this sampling is *biased*, and results in expression (13), rather than the straightforward  $I_w(q) = I(q)$ .

We now turn to the polydisperse configurations (figures 13, 14 and 15). Similarly to the monodisperse case, each spectrum is strongly peaked around a rather small value ( $0.05 \text{ nm}^{-1} \leq q_{\text{peak}} \leq 1.5 \text{ nm}^{-1}$ ). This again indicates pseudo-periodicity in the real space, which is due to the high compacity of the systems we generated. We note that the location of this peak,  $q_{\text{peak}}$  shifts towards the origin

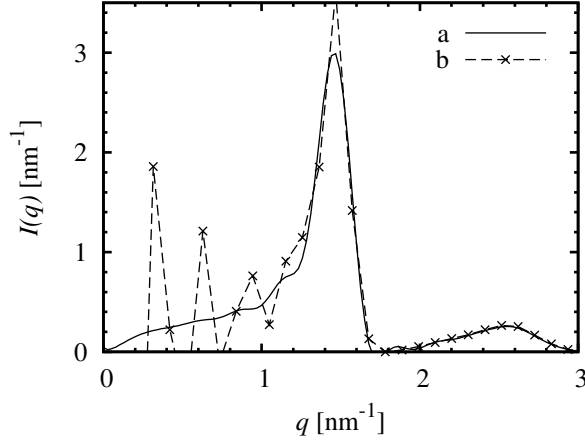


FIG. 12. The average scattering intensity  $I(q)$  of the monodisperse configurations `mono004`, `mono008`, `mono012`, `mono016` computed with the procedure proposed in this paper (a), and the procedure of Salacuse *et al.* [12, 32] (b). The latter is more sensitive than the former to ensemble size effects.

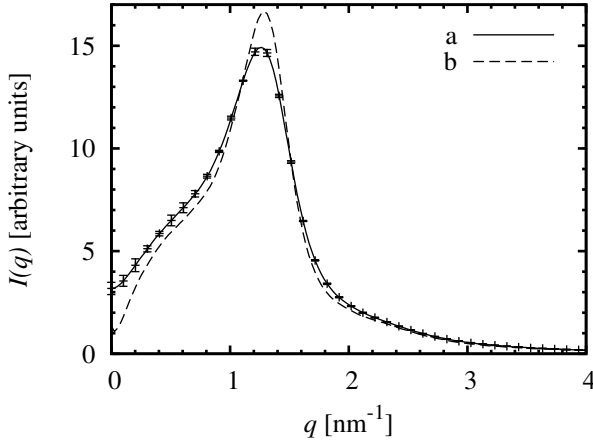


FIG. 13. The average blurred spectrum  $I_w(q)$  (a) of configurations `poly006`, `poly012`, `poly018`, `poly024` ( $\alpha = 0.20$ ), and the resulting deblurred spectrum  $I(q)$  (b).

( $q = 0$ ) as the polydispersity index  $\alpha$  increases. We were not able, however, to relate the location of the peak,  $q_{\text{peak}}$ , to the average radius of the particles, through a simple law such as  $q_{\text{peak}}\langle a \rangle \sim \text{Const.}$ ; therefore, the physical interpretation of the characteristic length-scale to which  $q_{\text{peak}}$  relates remains unclear. We also note that this peak tends to widen as the polydispersity index  $\alpha$  increases; this suggests that it would ultimately vanish for very high polydispersity.

Finally, similarly to the monodisperse case, it is possible to compare our procedure to the procedure of Lajovic *et al.* [29]. The results are not presented here, because they are similar to figure 12. This means that, when the compacity increases, the procedure of Lajovic *et al.* [29] becomes increasingly sensitive to size effects, while ours remains more robust to these effects. This result was

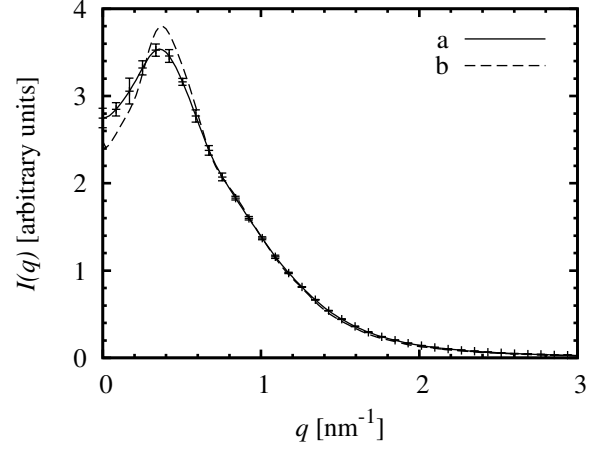


FIG. 14. The average blurred spectrum  $I_w(q)$  (a) of configurations `poly030`, `poly036`, `poly042`, `poly048` ( $\alpha = 0.51$ ), and the resulting deblurred spectrum  $I(q)$  (b).

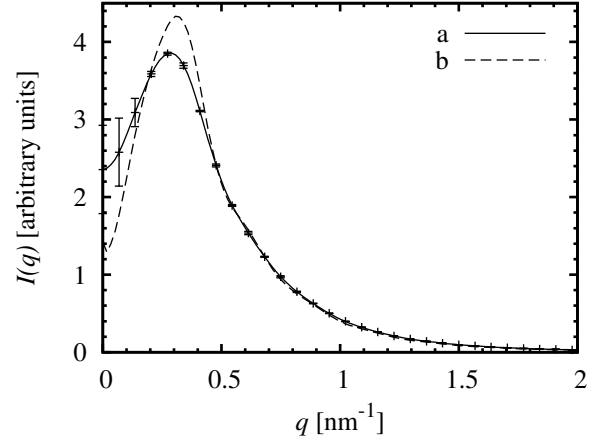


FIG. 15. The average blurred spectrum  $I_w(q)$  (a) of configurations `poly051`, `poly054`, `poly057`, `poly060` ( $\alpha = 0.78$ ), and the resulting deblurred spectrum  $I(q)$  (b).

somewhat expected from the analysis shown in figure 12, since the procedure of Lajovic *et al.* [29] coincides with the procedure of Salacuse *et al.* [12] in the monodisperse case.

## V. PERSPECTIVES: APPLICATION TO CEMENT PASTES

Investigation of cement pastes by small-angle scattering started in the mid-eighties [13, 53, 54]. Since this moment, it never failed to generate interest, as suggested by the large number of publications reporting on this subject [13, 14, 53–65]. One of the reasons for this keen interest is the fact that regardless of the precise composition or the age of the hardened cement paste, the scattering intensity  $I(q)$  invariably behaves as a fractional power of  $q$  in a wide range of this parameter.

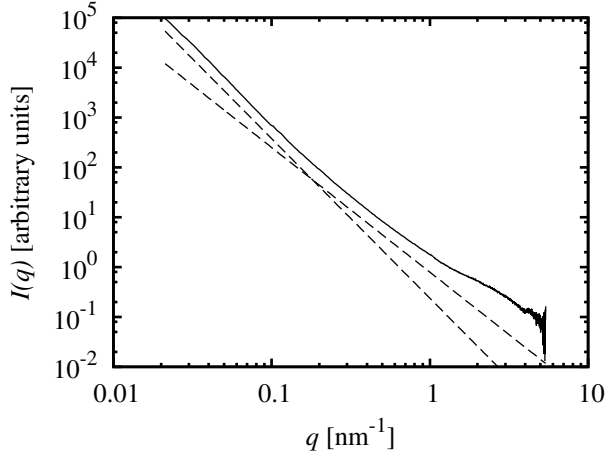


FIG. 16. SAXS data for a 1.5 year old CEM-I cement paste ( $w/c = 0.35$ ). Dashed lines represent the algebraic branches  $q^{-3.2}$  and  $q^{-2.5}$ . This data will serve as a reference to all subsequent numerical simulations.

Figure 16 is a typical example of the intensity scattered by a cement paste. In the present case, the specimen was made from CEM-I cement, cast in a cylindrical mold (70 mm  $\times$  140 mm), where it stayed for a year; the water-to-cement ratio was  $w/c = 0.35$ . The mold was then unsealed, and the specimen was wrapped in two layers of aluminum foil and stored at room temperature for six months; this sample preparation is routinely invoked at IFSTTAR[66] in order to maintain endogenous conditions. This sample (previously cut in 0.1 mm thick slices, and stored in water) was then submitted to small-angle X-ray scattering at the synchrotron Soleil (beamline Swing). The wave-length of the X-rays was 0.127 nm, and the sample-to-detector distance was successively 1.50 m then 6 m.

The resulting spectrum (see figure 16) clearly shows the existence of two power-law regimes, with a transition around  $q \simeq 0.2 \text{ nm}^{-1}$

$$I(q) \propto \begin{cases} q^{-(3+\epsilon_s)} & \text{for } q \leq 0.2 \text{ nm}^{-1}, \\ q^{-(2+\epsilon_v)} & \text{for } q \geq 0.2 \text{ nm}^{-1}, \end{cases}$$

with  $\epsilon_s \simeq 0.2$  and  $\epsilon_v \simeq 0.5$ , which is in good agreement with many other published results [14, 53, 55, 58, 59, 67, 68].

As stated in section I, the popular globular model of cement describes C-S-H as an assembly of near-spherical, densely packed particles, with a porosity around 0.30 – 0.35 [15]. Figure 10 –see also figure 17, (a)– shows that the scattering intensity  $I(q)$  of such monodisperse configurations behaves as  $q^{-4}$  (the so-called *Porod regime*) at high- $q$ , exhibits a strong correlation peak at  $q \simeq 2\pi/d$ , and ends in a pseudo-plateau with a negative slope at low- $q$ . Obviously, such a pattern does not fit the experimental data (figure 16), and the globular model must be revised.

A first option would be to consider a set of monodis-

perse discotic colloids (see figure 9). This would lead to  $I(q)$  behaving as  $q^{-2}$  at high- $q$ , in closer agreement with the experimental data. As shown in figure 9 however, for dense disordered packings, “colonar” order is observed on the length-scale of a few particle diameters. At larger length-scales, the system therefore reaches statistical homogeneity. In other words, similarly to assemblies of spherical particles,  $I(q)$  must exhibit a plateau at low- $q$ , which is confirmed by computations not presented here. Such a plateau is not observed experimentally.

A second option would be to consider interactions between particles. Obviously, attractive interactions between elementary particles must exist in cement pastes. Diffusion- and reaction-limited aggregation (DLCA and RLCA) processes are simple examples which are known to lead to mass fractal structures, the scattering intensity of which behaves as  $q^{-\nu}$  [1, 69, 70]. However, these structures are relatively open, and cannot account for the low porosity of C-S-H. Besides, applicability of DLCA and RLCA to the hydration of cement pastes is highly doubtful; packing-limited growth processes [71] would probably be more appropriate.

A third option is explored in the present work, where particle polydispersity is introduced. In the remainder of this section, the ability of the configurations considered in section IV to describe C-S-H is discussed. These assemblies of spheres share the same compacity  $f \simeq 0.64$ , which is representative of C-S-H in cement pastes [15], while their polydispersity index varies. All computed spectra (see figures 10 to 15) have been gathered in figure 17, where a logarithmic scale has been adopted. It should be recalled that after generation, each configuration is scaled so as to ensure that the (number-weighted) average radius  $\langle a \rangle$  of the globules is 2.5 nm (consistently with the globular model of C-S-H): all spectra therefore share the same reference length-scale, and direct comparison is meaningful.

Observation of figure 17 shows that in all instances, the beginning of the Porod regime ( $I(q) \propto q^{-4}$ ) follows closely the correlation peak, leaving virtually no space for an alternative power-law to develop. It is also observed that in the low- $q$  range, the spectra quickly reach a plateau. The computed spectra therefore share no common feature with the experimental intensity scattered by cement pastes. In other words, none of the systems considered in section IV can be regarded as convincing models of calcium-silicate hydrates in cement pastes.

One of the most remarkable features shared by all curves shown in figures 10 to 15 is the existence of a marked correlation peak. This peak tends to spread when the polydispersity index  $\alpha$  increases, which suggests to consider a system with a very wide particle size distribution. Widening this distribution tends to increase significantly the number of particles in numerical simulations. For this reason, we had to give up the generation of a random medium, and chose an Apollonius packing of spheres instead (see figure 18).

The particle size distribution of the Apollonius pack-



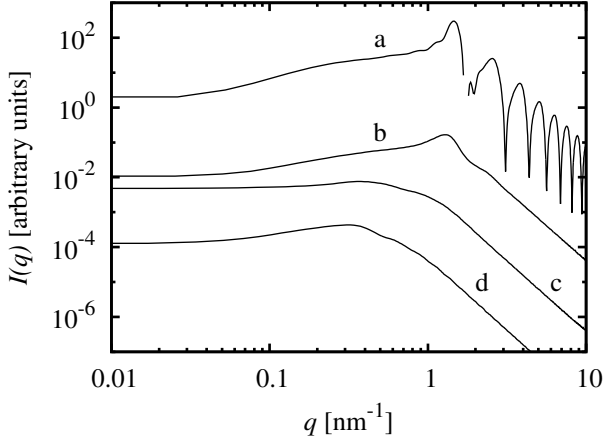


FIG. 17. Computed scattering intensity of configurations  $\alpha = 0$  (a),  $\alpha = 0.20$  (b),  $\alpha = 0.51$  (c),  $\alpha = 0.78$  (d). It should be noted that small-angle scattering spectra are generally known up to an arbitrary multiplicative constant (arbitrary translation along the vertical axis, in logarithmic scale). Therefore, the four curves presented here were spread vertically in order to improve legibility.

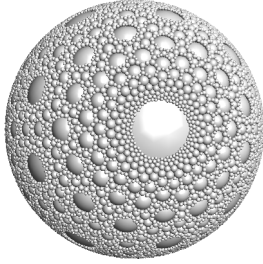


FIG. 18. Three-dimensional view of an apollonian packing of spheres.

ing is  $N(a) \propto a^{-d_v-1}$ , where  $N(a)da$  denotes the total number of spheres with radius between  $a$  and  $a + da$ , and  $d_v \simeq 2.47$  denotes the fractal dimension [72]. More details on the generation of the packing, as well as the computation of its small-angle scattering spectrum can be found in appendix E.

The resulting scattering intensity curve is shown in figure 19, where it is compared to an approximate calculation based on the chord-length distributions [73, eq. 40]

$$I(q) \simeq -\frac{\pi \Delta \rho^2 S_v}{q} \frac{d}{dq} \left[ \frac{1}{q^2} \text{Real} \left( \frac{(1 - \hat{f}_s(q))(1 - \hat{f}_p(q))}{1 - \hat{f}_s(q)\hat{f}_p(q)} \right) \right], \quad (33)$$

where  $S_v$  is the specific surface,  $f_s$  (resp.  $f_p$ ) is the probability density function of  $\mu$ -chords measured in the solid (resp. the pores), and  $\hat{f}_s$  (resp.  $\hat{f}_p$ ) its Fourier transform. The above approximate formula is valid, provided that the length of successive chords measured along the same random line are uncorrelated [73]. While this assumption would not be verified for the mildly polydisperse configu-

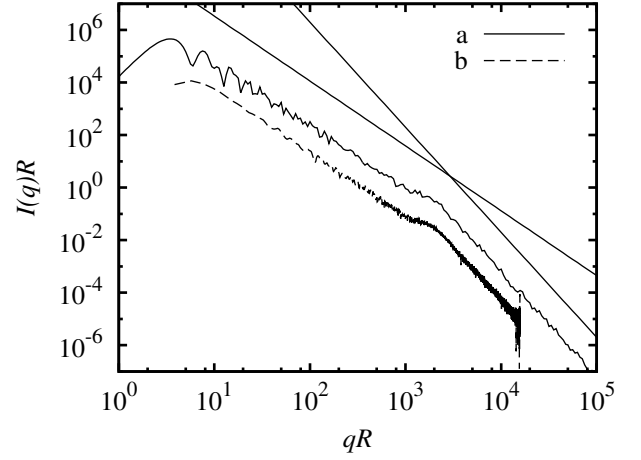


FIG. 19. Scattered intensity pattern of the Apollonius packing shown in figure 18, computed with the method proposed in this paper (a), and with the approximate formula (33) (b). The two curves are in excellent agreement, and match perfectly without rescaling; for the sake of readability, curve (b) has been translated vertically. The two straight lines represent the expected fractal ( $I(q) \propto q^{-2.47}$ , low  $q$ ), and Porod ( $I(q) \propto q^{-4}$ , high  $q$ ) regimes. In order to allow for the direct comparison of the two methods, both  $q$  and  $I(q)$  have been made dimensionless through multiplication by the external radius  $R$  of the packing; furthermore,  $\Delta \rho = 10^{10} R^{-2}$ .

rations considered in section IV, it is acceptable for highly polydisperse configurations, and our method is indeed in good agreement with equation 33 (see figure 19).

Observation of figure 19 shows that the scattering intensity curve comprises two power-law branches with a transition at  $qa_{\min} \simeq \pi$  ( $a_{\min}$ : radius of the smallest particles). At high- $q$ , the Porod regime  $I(q) \propto q^{-4}$  is retrieved, while at low- $q$ , the fractional power-law  $I(q) \propto q^{-2.47}$  is observed. The latter regime is consistent with the dimension  $d_v \simeq 2.47$  of the apollonian packing, which is a mass fractal [72], for which the scattered intensity must behave as  $q^{-d_v}$  [74–76].

Because of the absence of a correlation peak, the spectrum shown in figure 19 is much more satisfactory than all other spectra shown in figure 17, even if the exponent of the power-law does not match the values generally observed for cement pastes, and the resulting spectrum is therefore not fully consistent with experimental data.

The present calculation is encouraging, as it suggests that the scattering intensity of packings with carefully chosen power-law size distributions might exhibit the two features: absence of correlation peak, existence of power-law branches (other than the classical Porod regime), which are required to provide a convincing microstructural model of cement pastes.

To close this section, it should be noted that, due to its  $\mathcal{O}(N^2)$  complexity, the computation of the scattering intensity with the method of Lajovic *et al.* [29] would have been very difficult; indeed, on a standard laptop, the estimated required time was about 2, 200 days, while our

computation, which has  $\mathcal{O}(N)$  complexity, ran in only 2 days on the same computer.

## VI. CONCLUSION

In this paper, we proposed a new method for the computation of the scattering intensity of computer-generated microstructures. Although generally more CPU intensive than previously proposed methods for medium-sized configurations, it is more accurate at low- $q$ , and more robust with respect to ensemble size effects, particularly with dense configurations. It is also highly efficient in special situations where the spectrum must be updated following small alterations of the microstructure, or for very large configurations.

This method was validated against simple simulations, and subsequently applied to dense polydisperse distributions of hard spheres, for which a new generation procedure was also introduced.

Analysis of these computations shows that if the particle size distribution is too narrow, the small-angle scattering spectrum exhibits a sharp correlation peak, and no power-law regime (other than the Porod regime). Such microstructures are therefore not representative of hardened cement pastes.

By contrast, the correlation peak vanishes as the particle size distribution widens. Moreover, if the distribution follows a power-law, then the scattering intensity also follows a power-law.

This might suggest that the sizes of the C-S-H globules in hardened cement pastes are distributed according to a power-law. We find this conclusion questionable, since such distribution would lead to very wide polydispersity, which very few –if any– known elaboration processes could explain convincingly. Owing to Babinet’s principle, a dual hypothesis would be to assume that the sizes of the *pores* are distributed according to a power-law. This assumption will be explored in future work.

Even if their applicability to cementitious materials is questionable, dense assemblies of polydisperse particles with a power-law size-distribution are interesting models. The apollonian packing is a realization of such a system; however, the corresponding exponent of  $q$  in the small-angle scattering spectrum is not tunable. We therefore aim at developing a procedure for the generation of random configurations with tunable powers, and relate this power to that of the scattering intensity curve.

### Appendix A: Relationship between real and blurred spectra

In the present section, identity (13) is proved, under the assumption that the unit-cell  $\mathcal{U}$  is cubic, with sides of length  $L$ . Extension to unit-cells with unequal sides is straightforward. All simulations being carried out within the framework of the minimum image convention [42],

the fluctuations  $\eta$  of the scattering-length density can be decomposed in a Fourier series

$$\eta(\mathbf{x}) = \sum_{\mathbf{n} \in \mathbb{Z}^3} \hat{\eta}_{\mathbf{n}} \exp(i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{x}), \quad (\text{A1})$$

where  $\mathbf{k}_{\mathbf{n}} = (2\pi/L)\mathbf{n}$ , and  $\hat{\eta}_{\mathbf{n}}$  is the discrete Fourier transform

$$\hat{\eta}_{\mathbf{n}} = \frac{1}{|\mathcal{U}|} \int_{\mathbf{x} \in \mathcal{U}} \eta(\mathbf{x}) \exp(-i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{x}) d^3\mathbf{x}.$$

Substituting (A1) in (11), we find

$$A_{\text{w}}(\mathbf{q}, \mathbf{x}) = \sum_{\mathbf{n} \in \mathbb{Z}^3} \hat{\eta}_{\mathbf{n}} \hat{w}(\mathbf{q} - \mathbf{k}_{\mathbf{n}}) \exp[-i(\mathbf{q} - \mathbf{k}_{\mathbf{n}}) \cdot \mathbf{x}], \quad (\text{A2})$$

where the continuous Fourier transform  $\hat{w}$  of the characteristic function of the window  $\mathcal{W}$  has been introduced

$$\hat{w}(\mathbf{k}) = \int_{\mathbf{x} \in \mathbb{R}^3} w(\mathbf{x}) \exp(-i\mathbf{k} \cdot \mathbf{x}) d^3\mathbf{x}.$$

Then, by definition (12), the blurred spectrum  $I_{\text{w}}(\mathbf{q})$  is the volume average of the squared-modulus of  $A_{\text{w}}$ . Using (A2)

$$|A_{\text{w}}(\mathbf{q}, \mathbf{x})|^2 = \sum_{\mathbf{m}, \mathbf{n} \in \mathbb{Z}^3} \hat{\eta}_{\mathbf{m}}^* \hat{\eta}_{\mathbf{n}} \hat{w}(\mathbf{q} - \mathbf{k}_{\mathbf{m}}) \hat{w}^*(\mathbf{q} - \mathbf{k}_{\mathbf{n}}) \times \exp[-i(\mathbf{k}_{\mathbf{n}} - \mathbf{k}_{\mathbf{m}}) \cdot \mathbf{x}].$$

Upon integration on the unit-cell  $\mathcal{U}$ , the terms with  $\mathbf{m} \neq \mathbf{n}$  vanish, and

$$I_{\text{w}}(\mathbf{q}) = \frac{1}{|\mathcal{W}|} \sum_{\mathbf{n} \in \mathbb{Z}^3} |\hat{\eta}_{\mathbf{n}}|^2 |\hat{w}(\mathbf{q} - \mathbf{k}_{\mathbf{n}})|^2. \quad (\text{A3})$$

We now introduce the normalized correlation function  $\gamma_{\text{w}}(\mathbf{r})$  of the window  $\mathcal{W}$ , as well as its continuous Fourier transform  $\hat{\gamma}_{\text{w}}(\mathbf{k})$

$$\gamma_{\text{w}}(\mathbf{r}) = \frac{1}{|\mathcal{W}|} \int_{\mathbf{x} \in \mathbb{R}^3} w(\mathbf{x}) w(\mathbf{x} + \mathbf{r}) d^3\mathbf{x}, \quad (\text{A4})$$

$$\hat{\gamma}_{\text{w}}(\mathbf{k}) = \int_{\mathbf{r} \in \mathbb{R}^3} \gamma_{\text{w}}(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) d^3\mathbf{r}. \quad (\text{A5})$$

From the convolution theorem, we have  $\hat{\gamma}_{\text{w}}(\mathbf{k}) = |\mathcal{W}|^{-1} |\hat{w}(\mathbf{k})|^2$  and (A3) can be rewritten

$$\begin{aligned} I_{\text{w}}(\mathbf{q}) &= \sum_{\mathbf{n} \in \mathbb{Z}^3} |\hat{\eta}_{\mathbf{n}}|^2 \hat{\gamma}_{\text{w}}(\mathbf{q} - \mathbf{k}_{\mathbf{n}}) \\ &= \int_{\mathbf{r} \in \mathbb{R}^3} \left[ \sum_{\mathbf{n} \in \mathbb{Z}^3} |\hat{\eta}_{\mathbf{n}}|^2 \exp(i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{r}) \right] \\ &\quad \times \gamma_{\text{w}}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3\mathbf{r}. \end{aligned} \quad (\text{A6})$$

The quantity inside the square brackets is the autocorrelation of the fluctuations of the scattering-length density, which is defined by analogy with equation (5) (where the

ensemble average  $\langle \eta^2 \rangle$  is replaced by the volume average  $\overline{\eta^2}$

$$\gamma(\mathbf{r}; \mathcal{U}) = \frac{1}{\overline{\eta^2}} \frac{1}{|\mathcal{U}|} \int_{\mathbf{x} \in \mathcal{U}} \eta(\mathbf{x}) \eta(\mathbf{x} + \mathbf{r}) d^3 \mathbf{x},$$

where the notation  $\gamma(\mathbf{r}; \mathcal{U})$  instead of  $\gamma(\mathbf{r})$  is a reminder for the fact that the above autocorrelation is computed on a finite size simulation box, and therefore differs from the true autocorrelation of the random medium under consideration.

Obviously,  $\gamma(\mathbf{r}; \mathcal{U})$  has the same  $(L, L, L)$ -periodicity as  $\eta$ , and can also be decomposed in a Fourier series. Furthermore, from the convolution theorem

$$\gamma(\mathbf{r}; \mathcal{U}) = \frac{1}{\overline{\eta^2}} \sum_{\mathbf{n} \in \mathbb{Z}^3} |\hat{\eta}_{\mathbf{n}}|^2 \exp(i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{r}).$$

Combining with (A6), we find that

$$I_{\mathbf{w}}(\mathbf{q}) = \overline{\eta^2} \int_{\mathbf{r} \in \mathbb{R}^3} \gamma(\mathbf{r}; \mathcal{U}) \gamma_{\mathbf{w}}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3 \mathbf{r}.$$

If the unit-cell  $\mathcal{U}$  is large enough, then for  $|\mathbf{r}| < L/2$ , we have  $\gamma(\mathbf{r}; \mathcal{U}) = \gamma(\mathbf{r})$ , where  $\gamma(\mathbf{r})$  denotes the true autocorrelation (of infinitely large samples). Also, if  $|\mathbf{r}| > \text{diam } \mathcal{W}$  (diameter of the window), then  $\gamma_{\mathbf{w}}(\mathbf{r}) = 0$ . Therefore, provided that the diameter of the window is not greater than half the size of the unit-cell, we have for all  $\mathbf{r} \in \mathbb{R}^3$

$$\gamma(\mathbf{r}; \mathcal{U}) \gamma_{\mathbf{w}}(\mathbf{r}) = \gamma(\mathbf{r}) \gamma_{\mathbf{w}}(\mathbf{r}),$$

and

$$I_{\mathbf{w}}(\mathbf{q}) = \overline{\eta^2} \int_{\mathbf{r} \in \mathbb{R}^3} \gamma(\mathbf{r}) \gamma_{\mathbf{w}}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3 \mathbf{r}.$$

Unlike  $\gamma(\mathbf{r}; \mathcal{U})$  (which is periodic),  $\gamma(\mathbf{r})$  can be Fourier transformed (under the no long-range order assumption). Invoking again the convolution theorem, we finally find

$$I_{\mathbf{w}}(\mathbf{q}) = \frac{1}{(2\pi)^3} \int_{\mathbf{p} \in \mathbb{R}^3} \hat{\gamma}_{\mathbf{w}}(\mathbf{q} - \mathbf{p}) \overline{\eta^2} \hat{\gamma}(\mathbf{p}) d^3 \mathbf{p}.$$

For large enough simulation boxes,  $\overline{\eta^2} = \langle \eta^2 \rangle$ , and comparison with equation (4) shows that  $\overline{\eta^2} \hat{\gamma}(\mathbf{q})$  is indeed the scattered intensity  $I(\mathbf{q})$ . Therefore identity (13) is retrieved.

## Appendix B: Isotropic average of the blurred spectrum

In this section we give a proof of identity (17). Combining (13) and (16), the following integral must be simplified

$$I_{\mathbf{w}}(\mathbf{q}) = \frac{1}{32\pi^4} \int_{|\mathbf{n}|=1} \int_{\mathbf{p} \in \mathbb{R}^3} \hat{\gamma}_{\mathbf{w}}(\mathbf{q}\mathbf{n} - \mathbf{p}) I(\mathbf{p}) d^3 \mathbf{p} d^2 \mathbf{n}. \quad (\text{B1})$$

We first concentrate on the integration with respect to the unit vector  $\mathbf{n}$ . From (A5)

$$\begin{aligned} \int_{|\mathbf{n}|=1} \hat{\gamma}_{\mathbf{w}}(\mathbf{q}\mathbf{n} - \mathbf{p}) d^2 \mathbf{n} &= \int_{\mathbf{r} \in \mathbb{R}^3} \gamma_{\mathbf{w}}(\mathbf{r}) \exp(i\mathbf{p} \cdot \mathbf{r}) \\ &\times \int_{|\mathbf{n}|=1} \exp(-i\mathbf{q}\mathbf{n} \cdot \mathbf{r}) d^2 \mathbf{n} d^3 \mathbf{r}. \end{aligned} \quad (\text{B2})$$

Using the known identity

$$\frac{1}{4\pi} \int_{|\mathbf{n}|=1} \exp(-i\mathbf{z} \cdot \mathbf{n}) d^2 \mathbf{n} = \text{sinc} |\mathbf{z}|, \quad (\text{B3})$$

(B2) reduces to

$$\begin{aligned} \frac{1}{4\pi} \int_{|\mathbf{n}|=1} \hat{\gamma}_{\mathbf{w}}(\mathbf{q}\mathbf{n} - \mathbf{p}) d^2 \mathbf{n} &= \int_{\mathbf{r} \in \mathbb{R}^3} \gamma_{\mathbf{w}}(\mathbf{r}) \exp(i\mathbf{p} \cdot \mathbf{r}) \\ &\times \text{sinc}(\mathbf{q}\mathbf{r}) d^3 \mathbf{r}. \end{aligned}$$

Since the window  $\mathcal{W}$  is spherical,  $\gamma_{\mathbf{w}}(\mathbf{r})$  is a function of the norm  $r$  of  $\mathbf{r}$  only, and integration in spherical coordinates with respect to  $\mathbf{r}$  leads to

$$\begin{aligned} \frac{1}{4\pi} \int_{|\mathbf{n}|=1} \hat{\gamma}_{\mathbf{w}}(\mathbf{q}\mathbf{n} - \mathbf{p}) d^2 \mathbf{n} &= \int_0^{+\infty} \int_{|\mathbf{n}|=1} \exp(i\mathbf{r}\mathbf{p} \cdot \mathbf{n}) d^2 \mathbf{n} \\ &\times \gamma_{\mathbf{w}}(r) \text{sinc}(\mathbf{q}\mathbf{r}) r^2 dr, \\ &= \int_0^{+\infty} 4\pi r^2 \gamma_{\mathbf{w}}(r) \\ &\times \text{sinc}(\mathbf{p}\mathbf{r}) \text{sinc}(\mathbf{q}\mathbf{r}) dr, \end{aligned}$$

where (B3) has again been used. Substitution into (B1) gives

$$\begin{aligned} I_{\mathbf{w}}(\mathbf{q}) &= \frac{1}{(2\pi)^3} \int_{\mathbf{p} \in \mathbb{R}^3} I(\mathbf{p}) \int_{r \geq 0} 4\pi r^2 \gamma_{\mathbf{w}}(r) \\ &\times \text{sinc}(\mathbf{p}\mathbf{r}) \text{sinc}(\mathbf{q}\mathbf{r}) dr d^3 \mathbf{p}. \end{aligned}$$

Integration with respect to  $\mathbf{p}$  is again performed in spherical coordinates ( $\mathbf{p} = p\mathbf{n}$ ,  $|\mathbf{n}| = 1$ )

$$\begin{aligned} I_{\mathbf{w}}(\mathbf{q}) &= \frac{2}{\pi} \int_{p \geq 0} \int_{r \geq 0} \left[ \frac{1}{4\pi} \int_{|\mathbf{n}|=1} I(p\mathbf{n}) d^2 \mathbf{n} \right] r^2 \gamma_{\mathbf{w}}(r) \\ &\times \frac{\sin(pr)}{pr} \frac{\sin(qr)}{qr} dr p^2 dp, \end{aligned}$$

where the term in square brackets is the isotropic average  $I(q)$  of the true spectrum  $I(\mathbf{q})$ , and the above expression reduces to

$$\begin{aligned} q I_{\mathbf{w}}(q) &= \frac{2}{\pi} \int_{p \geq 0} \int_{r \geq 0} p I(p) \gamma_{\mathbf{w}}(r) \\ &\times \sin(pr) \sin(qr) dr dp. \end{aligned} \quad (\text{B4})$$

For spherical windows,  $\gamma_{\mathbf{w}}(r) = 0$  when  $r \geq 2R$ . When  $r \leq 2R$ ,  $\gamma_{\mathbf{w}}(r)$  is given by [see e.g. 77, equation (3.51)]

$$\gamma_{\mathbf{w}}(r) = 1 - \frac{3}{4} \frac{r}{R} + \frac{1}{16} \left( \frac{r}{R} \right)^3 \quad (r \leq 2R),$$

which is substituted into (B4)

$$qI_w(q) = \frac{2R}{\pi} \int_{p \geq 0} pI(p) \int_{x=0}^{x=2} \left(1 - \frac{3}{4}x + \frac{1}{16}x^3\right) \times \sin(pRx) \sin(qRx) dx dp.$$

Simple algebra finally shows that the above expression coincides with (17).

### Appendix C: Partial form factor of spherical particles

In this section, we propose a numerical method for the computation of the integral in equation (19), namely

$$G(\mathbf{q}, \mathbf{x}) = \int_{\mathbf{y} \in \omega} w(\mathbf{y} - \mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{y}) d^3\mathbf{y}, \quad (\text{C1})$$

when the particle  $\omega$  is partially included in the window  $\mathcal{W}$ , both being spherical. The spherical window  $\mathcal{W}$  is centered at  $\mathbf{x}$ , while the spherical particle is centered at  $\mathbf{x} + r\mathbf{n}$  ( $|\mathbf{n}| = 1$ ). Then  $G(\mathbf{q}, \mathbf{x})$  reads

$$G(\mathbf{q}, \mathbf{x}) = \exp(-i\mathbf{q} \cdot \mathbf{x}) \int_{\substack{|\mathbf{z}| \leq R \\ |\mathbf{z} - r\mathbf{n}| \leq a}} \exp(-i\mathbf{q} \cdot \mathbf{z}) d^3\mathbf{z},$$

where  $R$  (resp.  $a$ ) denotes the radius of the spherical window (resp. the spherical particle). Since the particle is partially included in the window, we have  $R - a \leq r \leq R + a$ . The above integral is best computed in cylindrical coordinates  $\mathbf{z} = \rho \cos \theta \mathbf{e}_1 + \rho \sin \theta \mathbf{e}_2 + \zeta \mathbf{e}_3$ , with

$$\mathbf{e}_3 = \mathbf{n}, \quad \mathbf{e}_2 = \frac{\mathbf{n} \wedge \mathbf{q}}{|\mathbf{n} \wedge \mathbf{q}|}, \quad \mathbf{e}_1 = \mathbf{e}_2 \wedge \mathbf{e}_3.$$

In this set of axes,  $\mathbf{q}$  has no component along  $\mathbf{e}_2$

$$\mathbf{q} = q_\perp \mathbf{e}_1 + q_\parallel \mathbf{e}_3, \quad q_\parallel = \mathbf{q} \cdot \mathbf{n}, \quad q_\perp = \sqrt{q^2 - q_\parallel^2},$$

while the joint conditions  $|\mathbf{z}| \leq R$  and  $|\mathbf{z} - r\mathbf{n}| \leq a$  reduce to  $\rho \leq \rho_{\max}(\zeta)$ , with

$$\rho_{\max}(\zeta)^2 = \begin{cases} a^2 - (\zeta - r)^2 & \text{if } r - a \leq \zeta \leq \zeta^*, \\ R^2 - \zeta^2 & \text{if } \zeta^* \leq \zeta \leq R, \end{cases}$$

where  $\zeta^* = (R^2 + r^2 - a^2) / (2r)$ . Combining the above equalities leads to the following expression

$$G(\mathbf{q}, \mathbf{x}) = \exp(-i\mathbf{q} \cdot \mathbf{x}) \times \int_{r-a}^R \int_0^{\rho_{\max}(\zeta)} \int_0^{2\pi} \rho \exp[-i(q_\perp \rho \cos \theta + q_\parallel \zeta)] \times d\theta d\rho d\zeta.$$

A closed-form expression for the integral with respect to  $\theta$  can be found in e.g. [78, 9.1.18]

$$G(\mathbf{q}, \mathbf{x}) = 2\pi \exp(-i\mathbf{q} \cdot \mathbf{x}) \times \int_{r-a}^R \int_0^{\rho_{\max}(\zeta)} \rho J_0(k_\perp \rho) \exp(-iq_\parallel \zeta) d\rho d\zeta,$$

where  $J_k$  is the Bessel function of  $k$ -th order and first kind. Similarly, integration with respect to  $\rho$  can be performed analytically [see e.g. 79, 5.52]

$$G(\mathbf{q}, \mathbf{x}) = \frac{2\pi}{k_\perp^2} \exp(-i\mathbf{q} \cdot \mathbf{x}) \int_{r-a}^R q_\perp \rho_{\max}(\zeta) J_1[q_\perp \rho_{\max}(\zeta)] \times \exp(-iq_\parallel \zeta) d\zeta.$$

The above formula shows that the volume integral (C1) reduces to a single integral, which is computed numerically. The interval of integration is decomposed in sub-intervals, delimited by the roots of the oscillatory integrand. On each of the sub-intervals, standard Gauss-Legendre quadrature (with typically 10 to 15 Gauss points) is used. It should be noted that to increase the efficiency of this scheme, approximate formulae provided by Abramowitz and Stegun [78, 9.4.4 and 9.4.6] are used for  $J_1$ .

### Appendix D: Fourier transform of the convolution kernel

The Fourier transform  $\hat{k}(x)$  of the convolution kernel  $k(q)$ , defined by (18) and (21), is given by the following two relations

$$\hat{k}(x) = \frac{3}{\pi} \hat{\varphi}\left(\frac{x}{2R}\right), \quad (\text{D1})$$

$$\hat{\varphi}(\omega) = \begin{cases} 0 & \text{if } |\omega| \geq 1, \\ \frac{1}{3}\pi \left(1 + \frac{3}{2}\omega - \frac{1}{2}\omega^3\right) & \text{if } -1 \leq \omega \leq 0, \\ \frac{1}{3}\pi \left(1 - \frac{3}{2}\omega + \frac{1}{2}\omega^3\right) & \text{if } 0 \leq \omega \leq 1, \end{cases} \quad (\text{D2})$$

where it is noted that (D2) is readily derived from the definition of the Fourier transform  $\hat{\varphi}$  of  $\varphi$

$$\hat{\varphi}(\omega) = \int_{-\infty}^{+\infty} \varphi(t) e^{-i\omega t} dt,$$

as well as the standard formula (to be understood in the sense of generalized functions)

$$\int_{-\infty}^{+\infty} \frac{e^{-i\omega t}}{t^n} dt = -i\pi \frac{(-i\omega)^{n-1}}{(n-1)!} \text{sgn}(\omega).$$

Substitution in (D1) provides a closed-form expression for  $\hat{k}(x)$ , from which it is apparent that  $\hat{k}(x) = 0$  for  $|x| \geq 2R$ .

### Appendix E: Generation of the apollonian packing, and computation of the scattering intensity

The generation of the configuration proceeds according to the efficient method outlined in [72]. The external radius of the packing is  $R = 1.0$ , and the radius of the largest spheres is  $a_{\max} \simeq 0.7R$ . All spheres with a radius

greater than  $a_{\min} = 10^{-3}R$  were generated; this led to an assembly of  $N = 5,974,835$  spheres.

Because the configuration at hand was not a realization of a random medium, the method described in section III had to be adapted in order to allow the computation of the small-angle scattering spectrum of the apollonian packing. More precisely, in the general method presented above, statistical homogeneity of the configurations required the use of many spherical windows. Indeed, there is no reason why the spherical window should be centered at a specific point.

In the present case, however, the configuration is not statistically homogeneous, and the center of the packing is

the obvious choice for the center of the spherical window  $\mathcal{W}$  (whose radius  $R$  is chosen so that  $\mathcal{W}$  coincides with the sphere enclosing the packing). Similarly to (19), the scattering amplitude is then computed as follows

$$A(\mathbf{q}) = \sum_{\beta=1}^N \Delta\rho_{\beta} v_{\beta} F_{\beta}(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{x}_{\beta}) - \Delta\bar{\rho} |\mathcal{W}| \exp(-i\mathbf{q} \cdot \mathbf{x}) F_{\mathbf{w}}(\mathbf{q}),$$

where it should be noted that since all particles are completely included in  $\mathcal{W}$ , equation (19) is greatly simplified. The scattering intensity is then retrieved from  $I(\mathbf{q}) = |\mathcal{W}|^{-1} |A(\mathbf{q})|^2$ . Finally, sampling the directions of  $\mathbf{q}$  allows the estimation of the isotropic average  $I(q)$ .

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